PREFACE SECOND EDITION

It is really a matter of great satisfaction and pleasure that the first edition of our book Physical Chemistry Part II has been well received and appreciated by all concerned. This has encouraged us to revise and enlarge the book within a year or so for better understanding to the average student of chemistry, keeping in veiw the suggestions received from teachers all over Rajasthan.

In the present edition, the general organisation of the previous edition has been retained, chapter seventh has been completely rewritten using very recent notations and conventions about cells. Many new changes have been incorporated in almost all the chapters, so that subject matter may be more interesting lucid and understandable. New diagrams have been included. More questions have been added. The present edition now completely meets all the requirements of 3rd year T.D.C. (Sc.) students of the University of Rajasthan, Jodhpur and Udaipur.

We gratefully acknowledge the suggestions given by our fellow colleagues for the improvement of the book.

Comments, criticism and suggestion if any would be gratefully accepted.

30th August, 1975 AUTHORS
(Krishna Janmashtami)

PREFACE FIRST EDITION

The revision of syllabus by the University of Rajasthan compels students preparing for B. Sc. (Pass) Examinations to consult several books for the prescribed syallabus. Our Physical Chemistry (Part I) covers the prescribed course for B. Sc. (Pass) Second Year. Now we are placing Physical Chemistry (Part II) in your hands which covers all the topics prescribed in the syllabus for B. Sc. (Pass) Third Year.

Following the trend set in Part I, the style employed is lucid and the subject matter has been presented in such a way that it helps in proper and easy understanding of various concepts. Sophisticated mathematical treatments have been avoided as far as possible. Standard sign and symbol conventions have been used. Various numerical problems, both solved and unsolved, have been given to familiarize the students with the principles involved. Objective type questions have been added at the end of each chapter to test the knowledge gained by the students.

We are thankful to Shri M.C. Gupta, Panchsheel Prakashan, Jaipur who took keen interest in publishing this book.

We shall be glad to receive comments and suggestions for the improvement of this book.

Aug. 15, 1973 AUTHORS

B.Sc. (Pass) Third Year Examination

Syllabus for Physical Chemistry

Note :—Two questions will be asked from Section 'A' and Four questions from Section 'B'.

Section 'A'

1. *Conductance and ionic equilibria :*

Conductivity and its determination, specific, equivalent, and molar conductivities, effect of dilution on conductivities, migration velocity of ions, transport number and its determination by Hittorf's method, moving boundary method and E.M.F. method, Kohlrausch's law, application of conductance measurement : determination of (i) degree of dissociation of weak electrolytes, (ii) solubility of sparingly soluble salts, (iii) hydrolysis constant, (iv) dissociation constant of weak acids and weak bases, (v) ionic product of water, (vi) conductometric titrations.

Ionic equilibria. Arrhenius theory of ionisations. Ostwald's dilution law, experimental verification of the law, limitation of Arrhenius theory, activity and activity coefficients, elementary treatment of Debye Huckel theory of strong electrolytes (no mathematical treatment), ionic strength.

2. *Electrochemistry* :

Galvanic cells, reversible and irreversible cells, Nernst solution pressure theory, electrical double layer, single electrode potential and half cells, electrode reactions, reversible electrodes (hydrogen electrode, silver, silver chloride electrode, Calomel electrodes). Oxidation reduction electrode (quinhydrone electrodes), glass electrode, standard electrode potential. electrochemical conventions, E.M.F. and its measurement, Nernst equation (no thermodynamic deduction) concentration cells, salts bridge. measurement of pH.

Section 'B'

3. *Thermodynamics* :

Second law of thermodynamics, entropy and its physical significance, molecular basis of entropy, work and free energy functions, Entropy changes in reversible and irreversible processes, Gibbs Helmholtz equation.

Crystalline and amorphous state, isotropy and anisotropy, symmetry, plane of symmetry, axis of symmetry and centre of symmetry, designation of crystals law of rational indices, classification of the crystals, spaces lattice, unit cells, simple, face centered and body centered cubic lattices, diffraction of x-rays by crystals, Bragg's equation, experimental methods (rotating crystal method, powder method) crystal structure of sodium chloride (Rock salt) KCl, graphite and diamond.

5. *Chemical Kinetics :*

Rate of reaction, specific reaction rate and its significance factors influencing rates of reaction, order and moleculatity of reactions, reaction of first order, second order and third order determination of order of reactions, importance of order in relation to mechanism of reactions, temperature dependence of reaction rates, activation energy, Arrhenius theory of reaction rates, activated complex.

6. *Spectroscopy :*

Dispersion of white light through prism, visible spectrum, optical spectroscope, nature of electromagnetic radiation, definition of terms wavelength frequency and wave number, absorption and emission spectra, basic principle of spectrometer (outlines only).

Electronic, vibrational and rotational transitions (No mathematical details). Brief outlines of ultra-violet visible spectroscopy (Lambert and Beer's law, extinction, molar extinction coefficient and, max, simple chromophores, auxochromes, K band, R-band, B-Band, bathochromic and hypsochromic shifts, hyperchromic, hypochromic effects), illustrated with simple examples; colour in transition metal compounds.

Brief outlines of infra-red spectroscopy, (modes of vibrations (symmetric, asymmetric. scissoring rocking, wagging and twisting vibrations), Absorption of simple and common functional groups C=O vibrations in ketones, carboxylic acids, amides and esters, O–H vibrations in alcohol, water and phenol, C–H vibrations in alkane, benzene and simple aromatic substituted compounds N–H vibrations in amines, C–X stretching vibration in halogen compounds (illustrated with simple examples).

Notes :—Numerical problems based on the above syllabus may be set in the question paper.

CONTENTS

1

Spectroscopy

Introduction.

Some of the experimental methods of physics have been used frequently to solve many problems in chemistry during the last sixty years. These physical methods have opened new areas of research in chemistry. They can be broadly divided into two main categories :

(*i*) Spectroscopic methods.
(*ii*) Diffraction methods.

We shall study about spectroscopic methods in this chapter, whereas diffraction methods will be dealt in the next chapter.

Apart from its lot of use in physics and chemistry, spectroscopy has contributed a great deal of knowledge regarding the changes taking place on earth as well as heavenly bodies. We have already learnt about the **atomic spectra** in our previous classes, hence we shall chiefly pay our attention to the **band spectra** of molecules in this chapter.

Dispersion of White Light and Visible Spectrum.

The simplest apparatus for producing a spectrum of white light is shown in Fig. 1·1. When a beam of light from a source F, *e. g.*, a tungsten filament lamp is selected by narrow slit S and allowed to fall on a prism P by a collimating lens L_1, a band of seven colours can be focussed on screen T with the help of an object lens L_2. *The phenomenon, in which white light is separated into various coloured components or wavelengths, is called* **dispersion**. The coloured components range from red, through orange, yellow, green, blue and indigo to violet. These colours diffuse gradually into each other. *The band of colours is known as* **spectrum**. **Spectra** *is the plural of spectrum.*

The Optical Spectroscope.

The complete optical system (as shown in Fig. 1·1.) *for producing and viewing the spectrum is known as* **optical spectroscope**. A simple spectroscope consists of the following parts :

1. *Source* F. Generally non-volatile incandescent solids radiate white light, hence a tungsten filament lamp is often used. Sunlight is also essentially white.

2. *Slit* S. It limits the width of entering beam. By the help of it the final images of various wavelengths can be made narrow. Hence slit should be straight and possess parallel and sharp edges. It should be kept clean because dust particles are reproduced in the images.

3. *Collimating lens* L_1. It bends the rays of light and makes them parallel before they enter the prism.

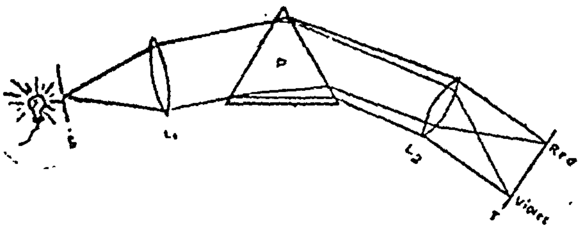


Fig 1·1. The Optical Spectroscope.

4. *Prism* P *or Grating*. The essential part of the spectroscope is the prism or diffraction grating, which is used as a dispersing medium. As the prism disperses the light, various components of different wavelengths are sent off in different directions.

5: *Object lens* L_2. The object lens brings the parallel rays of each componeht to focus and forms a sharp image of the slit in each component.

6. *Detector* T. The images of the slit in various coloured components can be viewed on the screen. Some spectroscopes use the magnifying eye-piece to see the images. In such cases, the object lens and the eye-piece form a small telescope.

There are various types of spectroscopes. *If a device is attached to a spectroscope to measure the wavelengh of light then, the instrument is called* **spectrometer**. *If the instrument makes photographic record of the spectrum, then it is called a* **spectrograph**. *A* **spectrophotometer** *is an instrument which makes use of photoelectric cell to provide a quantitative measure of light intensity at each wavelength.*

What is Spectroscopy ?

In this simple case of dispersion of wnite light, spectroscopy is the production and study of the spectrum of white light. Actually there are many forms of light or electromagnetic radiations such as X-rays. γ-rays, ultra-violet rays, infrared rays, cosmic rays, radic-waves apart from visible light. Spectroscopy extends to cover all these

radiations. Moreover, spectrum can be produced either by emission or absorption of radiations by matter. Hence we may define **spectroscopy** *as the study of the absorption and emission of all forms of electromagnetic radiations by matter.*

Nature of Electromagnetic Radiations.

If we remain near a fireplace, some sensation is felt on our skin and face even if we do not touch the flame. The same sensation is felt, if we stand in the noonday sun. It means that something is sent from the fireplace or the sun to our skin. We see television and listen to radio. Something is sent from the transmitting station which is converted into light and sound by our receiver. All these phenomena are the examples of the process called **radiations** by which the energy travels through space unaccompanied by transfer of matter. Generally the energy travels from the source in all directions like the *radii* of a circle, hence the name **radiation** is given. Visible light is the familiar kind of radiation.

In 1690, Huygens put forward the wave theory of light, according to which light travels in the form of waves. All waves like sound waves, water waves, and earthquake waves have the property of reflection, diffraction, and interference. Light waves were also shown to have all these properties. Before discussing the nature of light waves, it is proper to understand the various terms associated with a wave.

Wavelength. *The distance travelled by a wave during a complete cycel is called its* **wavelength.** In Fig. 1·2 the wavelength is shown by λ (*lambda*). It is expressed in *Angstroms* (Å) or *microns* (μ) or *millimicrons* ($m\mu$). These units are defined as below :

$$1 \text{ micron } (\mu) = 10^{-4} \text{ cm.}$$

$$1 \text{ millimicron } (m\mu) = \frac{1}{1000}\mu = 10^{-7} \text{ cm.}$$

$$1 \text{ Angstrom } (\text{Å}) = \frac{1}{10} m\mu = 10^{-8} \text{cm.}$$

Frequency. *The number of wavelength passing through any point* (say P in Fig. 1·2), *per second is known as* **frequency** of the wave. It is denoted by ν (nu) and expressed in *number of cycles per sec.* ν can be taken as a measure of energy according to the relation, $E = h\nu$, where $h = 6{\cdot}624 \times 10^{-27}$ erg sec.

Velocity. *The distance travelled by a wave in unit time is called its* **velocity.** If c is the velocity of a wave, then

$$c = \nu\lambda \tag{1·1}$$

It is expressed in *cm per sec.*

Wave number. *The number of wavelengths in one centimeter is known as* **wave number** *or* **kayser.** It is denoted by $\bar{\nu}$ and is given by

$$\bar{\nu} = \frac{1}{\lambda} \qquad ...(1\cdot2)$$

Putting the value of $1/\lambda$ from Eq. (1·1), we get

$$\bar{\nu} = \frac{\nu}{c} \qquad ...(1\cdot3)$$

It is expressed in cm^{-1}. $\bar{\nu}$ can be taken as a measure of energy according to the relation $E = h\nu = h\bar{\nu}c$.

In 1864 Maxwell published a series of papers regarding the nature of light. He showed theoretically that light is a movement of electric and magnetic waves at right angles to each other and also

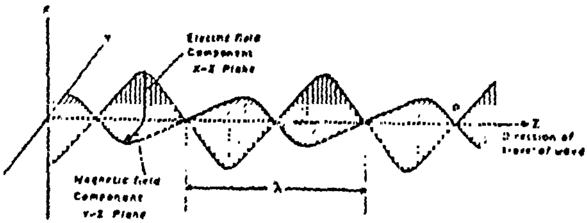


Fig 1·2. Nature of Electromagnetic Radiations.

to the direction of propagation of light as shown in Fig 1·2. If the light is travelling in the z direction, then electric and magnetic waves will be in the $(z-x)$ and $(y-z)$ planes respectively. Maxwell suggested that a vibrating electric charge could set up such waves. These waves travel with the speed of light. Thus, a wire carrying a high frequency current would send such variations in electric and magnetic felds in the form of waves. Hence they are called **electromagnetic waves.**

Visible light is one of the examples of electromagnetic waves. X-rays, ultraviolet rays, infrared rays, cosmic rays, and radiowaves are other examples of electromagnetic radiations. All these radiations are transmitted at the same speed, *i. e.*, $2{\cdot}99792 \times 10^{10}$ cm/sec but they differ in frequency and hence in wavelength also. *An ordered arrangement of radiations according to wavelength is known as* **electromagnetic spectrum.** The various regions of electromagnetic spectrum are shown in Table 1·1.

Table 1.1

The Regions of Electromagnetic Spectrum

S.N.	*Name of Radiation*	*Wavelength range* (Å)	*Frequency range (cycles/sec)*	*Energy range (ev)*	*Origin*	*Important uses*
1	Cosmic rays	$<10^{-2}$	$>10^{20}$	$>10^{7}$		
2	Gamma rays	10^{-2}—10	10^{20}—10^{17}	10^{7}—10^{5}	Nuclear energy transitions	Treatment of cancer
3	X-rays	1—10^{3}	10^{18}—10^{15}	10^{6}—10^{3}	Electronic energy transitions in inner shells	Treatment of skin diseases, crystal study
4	Ultra-violet rays	10^{2}—4×10^{3}	10^{16}—7.5×10^{14}	10^{3}—5	Electronic energy transitions in outer shells	Luminiscent lamps, molecular structure study
5	Visible light	4×10^{3}—8×10^{3}	$(7.5—3.8)\times10^{14}$	5—1.5	,,	Colorimetry, human sight
6	Infrared rays	8×10^{3}—2×10^{6}	3.8×10^{14}—10^{12}	1.5—10^{-2}	Vibrational and rotational energy transitions	Physical therapy, Molecular structure study
7	Microwaves	10^{6}—10^{9}	10^{12}—10^{9}	10^{-2}–10^{-3}	Electron spin orientation transitions	Radar, Short range communication
8	Radio-waves	10^{9}—10^{13}	10^{10}—10^{5}	10^{-3}–10^{-7}	Nuclear spin orientation transitions	Long range communication Television Broadcasting
9	A.C. Power line waves	$>10^{13}$	$<10^{5}$			

The intensity of radiation *is proporti*
photons per second that are propagated in th

matic radiation *consists of radiation of only one discrete wavelength,* while a **polychromatic radiation** *consists of radiations of several wavelengths.*

Emission and Absorption Spectra.

Spectra are mainly divided into two types : 1. Emission spectra. and 2. Absorption spectra. These two types are further subdivided as under :

- Spectra
  - Emission spectra
    - Continuous spectra
    - Discontinuous spectra
      - Line spectra
      - Band spectra
  - Absorption spectra
    - Continuous spectra
    - Discontinuous spectra
      - Line spectra
      - Band spectra

Emission spectra. *When the radiations emitted by a luminous source of light are examined directly by a spectroscope, then the spectra produced are known as* **emission spectra**. Visible spectrum obtained from a filament lamp or rays of the sun is a common example of emission spectrum.

Absorption spectra *When the light from a source is passed through an absorbing medium and the resulting radiations are examined by a spectroscope, then the spectra produced are known as* **absorption spectra.** Dark lines or bands are obtained on bright background in these spectra, because certain radiations are absorbed by the absorbing medium under investigation.

Both the emission and absorption spectra are subdivided into two classes on the basis of their appearance :

(*i*) Continuous spectra (*ii*) Discontinuous spectra.

Continuous spectra. In the visible spectrum we see that colours diffuse into each other gradually. Thus, the change in colour appears to be *continuous* and such spectra are called **continuous emission spectra.** Such spectra are obtained from incandescent solids, hot furnaces, hot iron, molten glass, etc. If a piece of pure red glass is put in the path of visible light, then red glass absorbs every radiation except the red one and the spectrum obtained in this way is called a **continuous absorption spectrum** of red glass.

Discontinuous Spectra. These spectra are not continuous in their appearance. They are further classified into

(*a*) Line spectra. (*b*) Band spectra.

Line spectra. *Line spectra consist of lines of definite wavelengths* and are given by gases and vapours of atoms. Hence they are also called **atomic spectra.** Line spectra of particular atoms, *e.g.*, Na-vapour, appear as bright lines on dark background in the emission spectra and as dark lines of the same wavelengths on the bright background in the absorption spectra. These lines can be grouped into various series. The sources of line spectra are vapours in flame and metallic arc.

Band spectra. *Band spectra appear as a group of bands which are sharply defined at one end and shaded off at the other end.* On closer examination with high resolving power instruments, it is seen that the bands actually consist of a large number of closely packed lines. When a substance giving a band spectrum of emission type is heated to such a high temperature at which its molecules break into atoms, then band spectrum disappears. This establishes that band spectra are produced by molecules, hence they are also called **molecular spectra.** They appear both in emission and absorption spectra. The sources of band spectra are carbon arc cored with metallic chlorides, bromides or fluorides and vacuum tube containing gases like CO_2, N_2 etc.

Basic Principles of Spectrometer.

We have already studied the optical spectroscope. Apart from this, there are various types of instruments for the production, observation and rocording of spectra. These instruments have received different names like spectrometer, photometer, spectrograph and spectrophotometer due to the various modifications already mentioned. However, the basic principle underlying these instruments can be understood with the help of spectrometer used for the study of absorption spectra. A flow-sheet representation of absorption spectrometer is shown in Fig. 1·3.

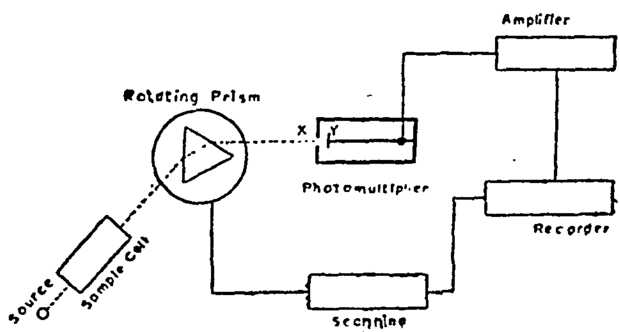


Fig. 1·3. Basic Arrangement of Instrumental Units in an Absorption Spectrometer.

Its main instrumental units are as follows :

1. Source. The function of source is to provide incident light of sufficient intensity and required region of wavelength. For visible.

near infrared and near ultraviolet regions, a glass enclosed tungsten filament is commonly used. Hydrogen (or deuterium) discharge lamp is adequate for work in ultraviolet region. Electrically heated rod of rare earth oxides at the temperature range 1500—2000°C is generally used for the work in infrared region. The beam from the source is focussed on the sample by means of lenses and mirrors.

2. Sample Cell. The sample cell is used to hold the compound under investigation. Cell is made of such a material which does not absorb the radiations of the source. The cell material is glass for visible light, quartz for ultraviolet, and alkali halides for infrared radiations. The sample in the cell absorbs characteristic wavelengths and passes them to the analyser.

3. Analyser. It consists of either a rotating prism or grating. The material of which a prism is made is the same as that used for sample cells in various regions of electromagnetic spectrum. The various wavelengths are separated by the prism. The differing wavelengths fall on the detector due to the rotating prism. The process is termed as *scanning*. It is synchronized with the recorder.

4. Detector. The detector converts radiant energy into electrical energy. Detectors are classified into two categories :

(*i*) *Thermal detectors* utilize the heating effect of current and are used for middle and infrared regions. Thermocouples, thermopiles, bolometer, etc., are examples of this type.

(*ii*) *Photo detectors* utilize the photoelectric effect and are used in visible, ultraviolet and near infrared regions. Photomultiplier is generally used in such work. It is extremely sensitive and fast in response. The beam from the analyser is focussed at the entrance slit X of the photomultiplier. When the beam falls on the light sensitive surface Y of the photomultiplier, electrons are emitted causing the formation of a small current. This current varies according to the intensity of the beam entering at X.

5. Recorder. The current is amplified by the amplifier and causes the pen recorder to move on a chart paper. *The graph on the chart paper showing the percentage absorption at various frequencies or wavelengths is thus obtained and is known as* **absorption spectrum** *of the sample.*

The basic principle for the instrumentation of emission spectra is similar to that of absorption spectra. The only difference is that the [illegible] ...ce. It is excited with thermal or electrical [illegible]. The emitted radiations are then analysed in the same way as described for absorption spectra. Photographic plate is generally used instead of detector and recorder.

BAND OR MOLECULAR SPECTRA

Just as line spectra have given valuable informations about the structure of atoms, in the same way band spectra have been found

much useful in the determination of molecular structure. We know that line spectra are simple and produced due to the transitions in the electronic energy in atoms. Band spectra are not so simple like line spectra. Actually its complex structure consists of a greater number of closely packed lines which appear as bands. This suggests that there must be not only transitions in electronic energy in molecules, but transitions in other forms of energy should also occur producing the complex structure of band spectra.

Origin of Band Spectra :

Electronic, Vibrational, and Rotational Transitions :

In order to account for the complex structure of band spectra, it has been postulated that when the radiations are emitted or absorbed by the molecules, then the transitions in its three forms of internal energy occur. These three forms of internal energy are :

1. **Electronic Energy.** It is due to the energy of electrons in a molecule, which exists in a number of energy levels as in case of atoms.

2. **Vibrational Energy.** It is due to the vibrations of atoms with respect to each other in a molecule as shown in Fig. 1·4 (*a*),

3. **Rotational Energy,** It is due to the rotation of molecule as a whole as shown in Fig. 1·4 (*b*).

We know that electronic energy in atoms is quantized. In the same way, the electronic, vibrational, and rotational energies of a molecule are also quantized. Thus, there are a number of energy

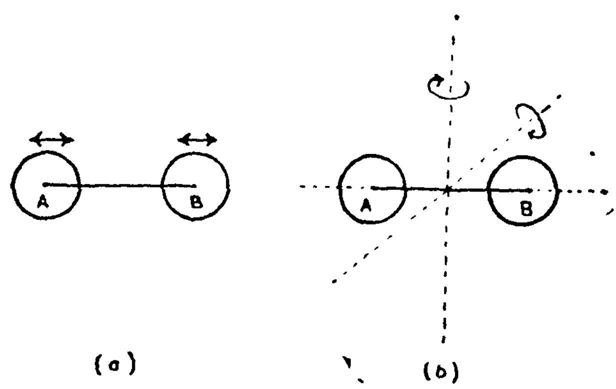


Fig. 1·4 (*a*) Vibration, and (*b*) Rotation, of a Diatomic Molecule AB.

levels with respect to each of the electronic, vibrational, and rotational energies in which the molecule can exist as shown in Fig. 1·5. The group of levels designated by principal quantum number n det. the electronic energy level of the molecule. Each of these electr

energy level is subdivided into vibrational energy levels designated by vibrational quantum number v and each of these vibrational energy level is further subdivided into rotational energy levels designated by rotational quantum number J

It is clear from Fig. 1·5 that the energy required for transitions in rotational energy levels of the molecule is least and it is increasingly greater for vibrational and electronic transition. If the molecule is excited with an energy as low as 0·005 *ev*, then only the transitions from one rotational level to another in the same vibrational level of the molecule will take place. There will be no vibrational or electronic transitions, because more energy is required for them. These pure rotational transitions will produce **rotational spectra.** Since the energies of the quanta involved in these transitions are very small, the rotational spectra are found in the high wavelength regions, *i.e.*, far infrared or microwave region.

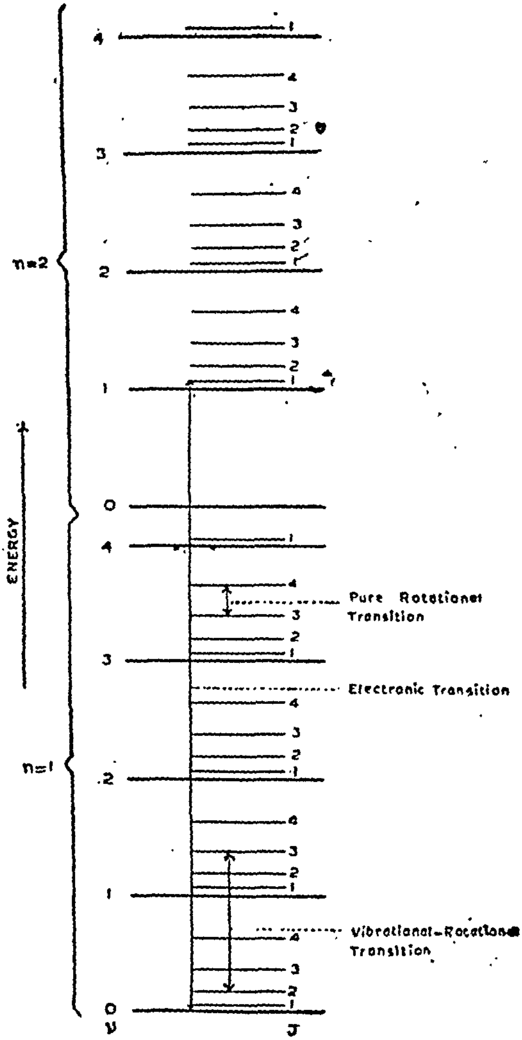


Fig. 1·5 Subdivision of Elecronic energy levels into Vibrational and Rotational energy levles of a Molecule.

If the molecule is excited with an energy of the order of 10^{-1} *ev*, then this energy is sufficient to cause the molecule to undergo transitions in vibrational levels within the same electronic level. As the transitions in vibrational levels are accompanied by rotational transitions, the spectra produced are called **vibrational rotational spectra.** It consists of lines due to vibrational transitions accompanied by the fine

structure due to rotational transitions. Vibrational rotational spectra are seen in near infrared region.

If the molecule is excited with still higher energy, *i. e.*, from 5. to 10 *ev*, then this energy is sufficient to bring about elctronic transitions. These electronic transitions are accompanied by vibrational transitions, which in turn are accompanied by rotational transitions. This results into the production of **electronic spectra** consisting of line due to electronic, vibrational, and rotational transitions. Each electronic transition produces an **electronic band**. A number of such electronic transitions will produce a **band system** composed of various electronic bands. The series of such band systems is **band spectra.** It appears in visible and ultraviolet regions.

Classification of Band Spectra.

Band spectra are classified either according to the molecular energies involved in the production of spectra or according to the region of electromagnetic spectrum in which they are seen. Fortunately, the types of band spectra obtained on the basis of these two criteria are similar as given below :

1. Rotational Spectra Rotational spectra are produced due to the transitions in the rotational energy of the molecule only. As they are seen in the microwave region of the electromagnetic spectrum, their study is termed as **microwave spectroscopy.**

2. Vibrational Rotational spectra. Vibrational rotational spectra are produced due to the simultaneous transitions in the vibrational and rotational energies of the molecule. As they are seen in the infrared region of the electromagnetic spectrum, their study is termed as **infrared spectroscopy.**

3. Electronic Spectra. Electronic spectra are produced by the simultaneous transitions in the electronic, vibrational and rotational energies of the molecule. As they are seen in the ultraviolet and visible region of the electromagnetic spectrum, their study is termed as **ultraviolet and visible spectroscopy.**

These different types of spectra differ in instrumentation also.

ULTRAVIOLET AND VISIBLE SPECTROSCOPY

Ultraviolet and visible spectroscopy is the study of electronic spectra which are found in the wavelength region 100—8000 Å of the electromagnetic spectrum. It has been found that the transitions in the energy levels of outer shell electrons are responsible for the production of spectra in this region.

Instrumentation.

The general outline of the apparatus used has already been given in Fig. 1·3 The most suitable source of light is the hydrogen discharge lamp for ultraviolet region and tungsten filament lamp for visible region. The light from the source is dispersed into various wavelengths by prism or grating. The prism material is quartz for ultraviolet and glass for visible region. The U. V. spectra of compounds are

generally determined either in vapor phase or in solution. The compound under investigation should be dissolved in that solvent which does not absorb in that region. Ethyl alcohol (95%) is commonly used for this purpose. The dilute solution of the compound is placed in sample cell made of quartz for ultraviolet region and glass for visible region. Visible and ultraviolet spectra are generally recorded as absorption spectra.

In order to get useful information from these absorption spectra it is essential to have a clear understanding of the fundamental laws of light absorption and various terms used therein.

Fundamental Laws of Light Absorption

1. Lambert's Law. This law gives a relationship between the extent of light absorption and the thickness of the absorbing material. According to this law, *when a parallel beam of monochromatic light enters perpendicularly into a homogeneous absorbing material, the rate of decrease in the intensity of light with the length of the light path through the absorbing medium is proportional to the intensity of the incident beam.* Mathematically,

$$\frac{-dI}{db} \propto I$$

or
$$\frac{-dI}{db} = kI \qquad ...(1{\cdot}4)$$

where I is the intensity of beam, dI is the infinitesimal change in intensity when the light has travelled the infinitesimal length db through the absorbing material and k is the proportionality constant, known as **absorption coefficient**. The negative sign on left hand side indicates that I decreases as b increases. Eq. (1·4) can be written as

$$\frac{-dI}{I} = k\,db \qquad ...(1{\cdot}5)$$

Eq. (1·5) can be integrated with the boundary condition that $I=I_0$ at $b=0$, *and* $I=I$ at $b=b$.

Thus,

$$\int_{I_0}^{I} \frac{-dI}{I} = \int_{0}^{b} k\,db$$

or
$$\ln \frac{I_0}{I} = kb$$

or
$$2{\cdot}303 \log_{10} \frac{I_0}{I} = kb$$

or
$$\log_{10} \frac{I_0}{I} = Kb \qquad ...(1{\cdot}6)$$

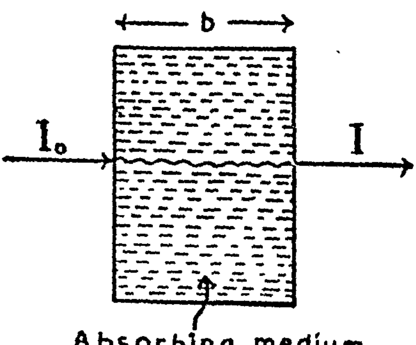


Fig. 1·6. Light Absorption

where I_0 is the intensity of inci-

dent beam, when b is zero, and I is the intensity when the beam has travelled the thickness b of absorbing material and $K = k/2{\cdot}303$ is called **extinction coefficient**. The term $\log_{10} \frac{I_o}{I}$ is known as **extinction** or **absorbance** or **optical density** and is denoted by A. Thus,

$$A = \log_{10} \frac{I_o}{I} \qquad \ldots(1{\cdot}7)$$

Alternatively, **Lambert's law** can be stated as :

When a parallel beam of monochromatic light enters perpendicularly into homogeneous absorbing medium, the absorbance is directly proportional to the length of the path traversed by the beam.

2. **Beer's Law.** If the absorbing material is in the form of a dilute solution, the relationship between the intensities of incident and transmitted light is given by Beer's law. According to this law, *When a parallel beam of monochromatic light enters perpendicularly into a dilute solution, the absorbance is directly proportional to the concentration of solution.* Mathematically,

$$A = \log_{10}\frac{I_o}{I} = K'c \qquad \ldots(1{\cdot}8)$$

where K' is a constant and c is the concentration of solution.

3. **Beer-Lambert Law.** It is the combined from of Beer's law and Lambert's law. According to it, *when a parallel beam of monochromatic light enters perpendicularly into a dilute solution, the absorbance is directly proportional to the number of solute molecules in the path travelled.* If the absorbing material is in the form of solution, then the number of its molecules in the path of light is proportional to the molar concentration c of the material as well as the length of path b (cm). Thus the mathematical form of Beer-Lambert law is

$$A = \log\frac{I_o}{I} = \epsilon cb \qquad \ldots(1{\cdot}9)$$

where ϵ is a constant called **molar extinction coefficient** or **molar absorptivity**. If $c = 1$ and $b = 1$ in Eq. (1·8), then

$$\text{Extinction } A = \epsilon$$

Thus, **molar extinction coefficient** can be defined as *the extinction due to 1 cm thick layer of solution whose molar concentration is unity*. It is characteristic of a compound provided the wavelength of light and temperature are kept constant.

Transmittance. If T is the transmittance of a s[illegible] it is defined as

$$T = \log \frac{I}{I_o} \qquad \ldots(1{\cdot}10)$$

From Eqs. (1·9) and (1·10) we get,

$$T = -\epsilon cb \qquad \ldots(1{\cdot}11)$$

It is clear from the Eq. (1·11) that greater is the value of extinction lesser is transmittance.

Example 1.1. *The molar extinction coefficient of a substance is 14000 at its λ_{max}. With a cell of 1 cm thickness, what is the molarity of the substance if spectrophotometer gives the absorbance reading as 0·85.*

Solution. We know that

$$A = \epsilon cb$$

or

$$c = \frac{A}{\epsilon b}$$

Here $A = 0{\cdot}85$, $\epsilon = 14000$, and $b = 1$ cm

$$\therefore \quad c = \frac{0{\cdot}85}{14000 \times 1}$$

$$= 6{\cdot}07 \times 10^{-5} M$$

Absorption Spectrum and λ_{max}. Characteristic Properties of a compound.

The quantity absorbance or transmittance for a compound is directly measured by spectrophotometers at various wavelengths. If a solution of known cencentration is put in a cell of known thickness, then the values of molar extinction coefficient ϵ for the given compound at vaious wavelengths are obtained from the values of absorbance or transmittance. *The curve showing the variation of A or ϵ with wavelength for a given concentration of solution and thickness of the cell is known as* **absorption spectrum** of the compound. Just as two compounds may have the same value of melting point or boiling point, but rarely do they have the same values of both melting and boiling points, in the same way, no two compounds can have the same set of ϵ values at various wavelengths, *i. e.*, they cannot have the same absorption spectrum. Thus, absorption spectrum is the characteristic property of the compound. *The wavelength corresponding to maximum absorption can be known from the absorption spectrum and is termed as λ_{max}*, which is likewise the characteristic property of a compound.

Deviations from Beer-Lambert's Law.

Since molar extinction coefficient is constant for a solute, it is clear from Eq. (1·9) of Beer-Lambert's law that the extinction *A* of its solution should remain the same, provided the product *cb* is kept contant. Thus, the extinction of a 1 cm thick layer of *M* solution should be the same as that of 5 cm thick layer of *M*/5 solution. This

is not found in practice always, because ϵ varies with concentration of the solution in many cases. These *deviations* may be caused by any of the following factors :

(*i*) Ionization of solute.
(*ii*) Association of solute.
(*iii*) Fluorescence of solute.
(*iv*) Poor transmission of solvent.

Hence we should not take the validity of Beer-Lambert's law as granted in spectrophotometric work. It is a usual practice to confirm it over the entire range of concentration to be used before proceeding to spectrophotometry. While confirming the Beer-Lambert's law the following **limitations** of the law must be kept in mind :

(*a*) A parallel beam of monochromatic radiations should be used.

(*b*) Temperature should remain constant.

(*c*) The solution to be used should be dilute.

(*d*) The solute should not exist in chemical equilibrium with the solvent.

Chromophores

It has been recognised since long that the colour of a molecule is due to one or more unsaturated groups present in it. These groups are called chromophores. They exhibit characteristic absorption in ultraviolet and visible regions. Thus, a **Chromophore** may be defined as *an isolated functional group not in conjugation with any other group which imparts colour to a compound absorbing characteristic wavelength in ultraviolet and visible regions*. Typical examples of chromophores are C=C, C≡N, C=O, N=N, C=S, and N=O in the order of increasing power of imparting colour. If a number of compounds have the same functional group without any complicating environmental factors, then all of them will absorb at nearly the same wavelength. Their molar extinction coefficients will also be nearly the same. Thus, it is clear that the functional group in an unknown compound can be found, if its absorption spectrum is correlated with the data for known compounds.

Auxochromes.

Those groups which do not impart colour to a compound by themselves, but increase the colouring power of a chromophore when attached to them are called **auxochromes**. These groups show characteristic absorption below 2000 Å by themselves. When they are attached to a chromophore, they usually cause a shift in the absorption towards longer wavelength. Auxochromes also increase the intensity of absorption. For example, the characteristic absorption of *trans p*-ethoxyazobenzene is shifted 650 Å towards longer wavelength

and is about doubly intense as compared to the corresponding absorption of trans-azobenzene. Typical examples of auxochromes are OH, NH_2, NR_2, OR, CH_3 and Br. All auxochromes contain non-bonding electrons. The action of an auxochrome is due to the electronic transitions involving these non-bonding electrons. It will be discussed in detail in the next section.

Origin of Electronic Absorption Bands :

K-Band, B-Band, and R-Band

The origin of bands in the electronic spectra (ultraviolet and visible spectra) is due to the transitions in the electronic energy of the valence electrons. These valence electrons exist in atomic orbitals in atoms. When a molecule is formed, then valence electrons taking part in bond formation exist in **bonding orbitals.** Electrons which form σ-bonds are called σ- **electrons** and those which form π-bonds are called **π-electrons.** Some unshared electrons in a molecule do not take part in any bond formation and exist in **non-bonding orbitals.** Such electrons are called **n-electrons.** Apart from these, there ar · higher energy levels termed as **anti-bonding orbitals** by molecular orbital theory. The anti-bonding orbitals associated with σ- and π-bonds are called σ^* (sigma star) and π^* (pi star) **orbitals.** As n-electrons do not take part in bonding orbitals, no anti-bonding orbital is associated with them. Anti-bonding orbitals are vacant in the ground state of the molecule, but they are filled in excited states.

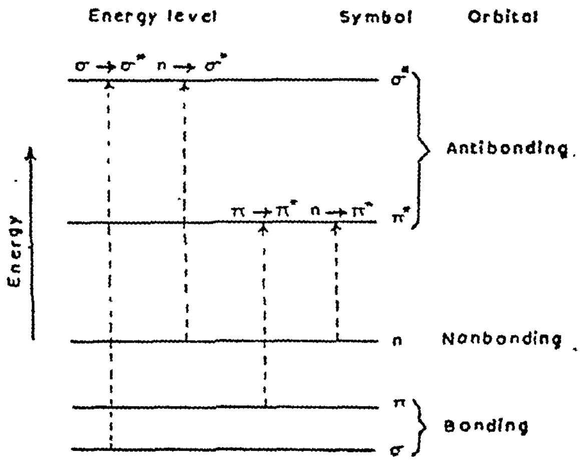


Fig. 1·7. Schematic Arrangement of Electronic Energy Levels and Possible Transitions.

A schematic arrangement showing the energy levels of all these orbitals is shown in Fig. 1·7. When a molecule absorbs in ultraviolet and visible regions, then the transitions that occur in electronic energy levels are (*i*) $\sigma \rightarrow \sigma^*$ (*ii*) $n \rightarrow \sigma^*$ (*iii*) $\pi \rightarrow \pi^*$ and (*iv*) $n \rightarrow \pi^*$ as shown in Fig. 1·7.

(*i*) $\sigma\rightarrow\sigma^*$ **Transitions.** These transitions require high energy as shown in Fig. 1·7. Hence the molecules undergoing these transitions generally absorb in the far ultraviolet region. Compounds in which all the valence electrons form σ bonds absorb in this region, *e. g.*, CH_4 absorbs at 125 $m\mu$.

(*ii*) $n\rightarrow\sigma^*$ **Transitions.** Those saturated compounds which contain singly bonded groups with atoms having non-bonding electrons undergo $n\rightarrow\sigma^*$ transitions. The atoms containing non-bonding electrons are generally O, N, S, and halogens. As $n\rightarrow\sigma^*$ transitions require lesser energy than $\sigma\rightarrow\sigma^*$ transitions (Fig. 1·7), the absorption takes place at comparatively higher wavelengths in ultraviolet region. For example, such transitions occur in trimethyl amine, methyl iodide and methyl alcohol and the corresponding λ_{max} values are 227 $m\mu$, 258 $m\mu$, and 183 $m\mu$ respectively.

(*iii*) $\pi\rightarrow\pi^*$ **Transitions.** As is clear from Fig. 1·7, $\pi\rightarrow\pi^*$ transitions are of intermediate energies, *i.e.*, the energy required for these transitions is lesser than required in $n\rightarrow\sigma^*$ transitions, but more than required in $n\rightarrow\pi^*$ transitions. Thus, the compounds undergoing these transitions generally absorb in ultraviolet or visible regions. In compounds containing unconjugated double bond, the $\pi\rightarrow\pi^*$ transitions cause absorption in ultra-violet regions. For example, $\pi\rightarrow\pi^*$ transitions cause absorption at, $\lambda_{max}=180\ m\mu$, in

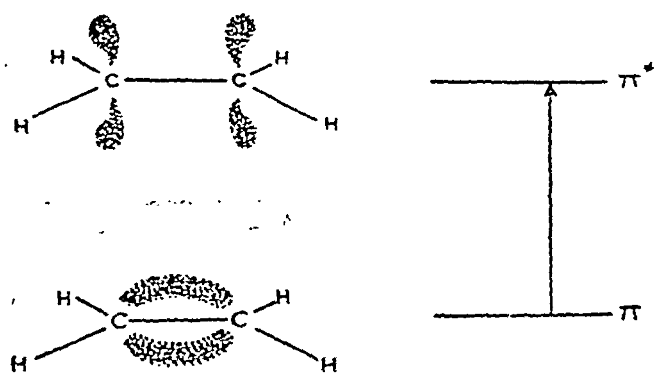


Fig. 1·8. $\pi\rightarrow\pi^*$ Transition in Ethylene.

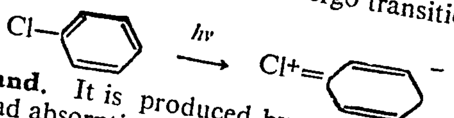
ethylene as shown in Fig. 1·8. Further, $\pi\rightarrow\pi^*$ transition in organic compounds may produce the following two types of bands.

(*a*) **K-Band.** It is produced by organic compounds containing conjugated system of double bonds, e.g., butadiene. The term **K-band** is derived from the German word *konjugierte*. This band is known as **K-Band** in British school and **primary band** in American school. Conjugation causes shifting of the band towards longer wavelengths and increases its intensity. Moreover, extension of conjugation causes regular shifts to longer wavelength side and higher molar absorptivities as shown in Table 1·2.

Table 1·2
K-Band in Conjugated Molecules

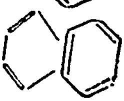
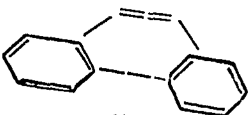
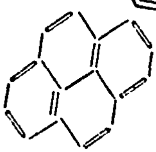
Compound	K-Band	
	λ_{max} ($m\mu$)	$\epsilon_{max} \times 10^3$
$CH_2{=}CHCH{=}CH_2$	217	21
$CH_3CH{=}CHCHO$	217	16
$CH_2{=}CHCH{=}CHCH{=}CH_2$	258	35
$CH_3\ (CH{=}CH)_4\ CH_3$	296	52

The molecules producing K-band undergo transitions to polar excited states as given below :



(*b*) **B-Band.** It is produced by aromatic compounds. There appears a broad absorption band in benzene with λ_{max} at 254 $m\mu$. It contains a fine structure due to vibrational sub-levels accompanying he electronic transition. If a chromophore is attached to a benzene ng, the B-bands appear at longer wave-lengths than the more intense -bands. When the vibration of the molecule is such that the symetry of aromatic ring is destroyed, then transition of molecule to mopolar excited state results in the production of B-band. This nd is known as **B-band** in British School and **secondary band** in nerican School. This band occurs at larger wavelengths and wit intensity as shown in Table 1·3.

Table 1·3
B-Band in Aromatic Compounds

Compound with structure		B-Band	
		λ_{max} ($m\mu$)	ϵ_{max}
e		254	204
ene		312	250
rene		330	250
		352	630

A compound may show both K-band and B-band, *e.g.*, benzene and monosubstituted benzenes like C_6H_5I, C_6H_5OH, $C_6H_5CH_3$ etc. show both K- and B-bands as shown in Table 1·4.

Table 1·4
Compounds showing both K-band and B-band

Compound	K-Band		B-Band	
	λ_{max} ($m\mu$)	ϵ_{max}	λ_{max} ($m\mu$)	ϵ_{max}
C_6H_6	203·5	7400	254	204
C_6H_5I	207	7000	257	700
C_6H_5OH	210·5	6200	270	1450
$C_6H_5CH_3$	206·5	7000	261	225
C_6H_5CN	224	13000	271	1000
$C_6H_5NH_2$	230	8600	280	1430

(*iv*) $n \rightarrow \pi^*$ **Transitions : R-Band.** In a molecule [illegible] with *n*-electrons has an unsaturated linkage with [illegible] $n \rightarrow \pi^*$ transitions take place. These transitions require less energy (Fig. 1·7), hence the bands are observed towards longer wavelengths *i.e.*, in near ultraviolet or visible regions with low [illegible]. These bands are called **R-bands.** Many chromophores [illegible] —N=N—, C=S exhibit $n \rightarrow \pi^*$ transitions, *e.g.*, [illegible] butane absorbing at 277 $m\mu$ and 665 $m\mu$ [illegible] R-bands. These bands are characterised by low ϵ [illegible] than 100. When additional bands like K- and B-[illegible] compound, R-band is shifted to longer wavelength.

Effect of Substituents and Solvents

The effect of substituents and solvents [illegible] been extensively studied. The [illegible]

1. **Bathochromic Shift.** [illegible] OH, CH_3, NH_2 etc., is substituted [illegible] tion-band is shifted to longer wavelength [illegible] *bands towards longer wavelength* [illegible] *effect are known as* **bath**[illegible] the λ_{max} for C_6H_6 and C_6[illegible] Thus the substitution [illegible] shift in the absorption [illegible] causes bathochromic shift.

2. **Hypsochr**[illegible] acetyl group is sub[illegible] is shifted to shorter wavelength [illegible] *to shorter wavelength* [illegible]

known as **hypsochromic** or **blue shifts.** If CH_2 group is introduced in an unsaturated chain of an organic compound, then conjugation is destroyed and absorption band of the compound is shifted to shorter wavelengths.

3. Hyperchromic Effect. *If a substituent group causes increase in the intensity of band, then the effect is called* **hyperchromic effect.** The increase in the intensity of absorption band is due to the fact that the substituent group causes the increase in the molar extinction coefficient ϵ of the compound. As for example, the ϵ_{max} for C_6H_6 and $C_6H_5CH_3$ are 204 and 225 respectively for B-band. Thus, the substitution of CH_3 group in C_6H_6 causes hyperchromic effect.

4. Hypochromic Effect *If a substituent group causes the intensity of the band to decrease, then the effect is called* **hypochromic effect.** As for example, ϵ_{max} for C_6H_6 and C_6H_5Cl are 204 and 190 for B-band. Thus, substitution of Cl causes hypochromic shift.

Colour of Transitional metal Compounds.

Many complex ions of transitional elements and their compounds are coloured in solution, *e.g.*, $[Cu(NH_3)_4]^{2+}$ is blue and $[Ti(H_2O)_6]^{3+}$ is purple. Transition metal ions contain incomplete *d*- orbitals, which are responsible for the colour of the ion. The correlation between the colour of the ion and the presence of incomplete *d*-orbital in it is shown in Table 1·5.

Table 1·5

Colour of Transitional Metal Ion Hydrates

Metal ion	*Total number of electrons in d-orbital*	*Number of unpaired electrons in d-orbital*	*Colour*
K^+, Ca^{2+}, Sc^{3+}	0	0	Colourless
Ti^{3+}	1	1	Purple
V^{3+}	2	2	Green
Cr^{3+}	3	3	Violet
Gr^{2+}	4	4	Blue
Mn^{2+}	5	5	Pale pink
Fe^{2+}	6	4	Green
Co^{2+}	7	3	Pink
Ni^{2+}	8	2	Green
Cu^{2+}	9	1	Blue
Zn^{2+}, Ga^{3+}	10	0	Colourless

It is clear from Table 1·5 that metal ions which contain vacant or completely filled *d*-orbital are colourless, while those having partially filled *d*-orbitals are coloured.

All the five *d*-orbitals in a free atom or ion of transitional element are of equal energy in the absence of an external electric or magnetic field and the electron can jump from one of these *d*-orbitals to other without emission or absorption of energy. When these ions form complexes, the central metal ion is attached to negative ions such as Cl^-, Br^-,CN^- or neutral polar molecules such as H_2O, NH_3, etc., called **ligands**. The number of ligands which are attached to the central ion depends upon the coordination number of the ions. Ths number varies from 2 to 8 in different compounds of transitional elements. In the complexes the five *d*-orbitals of the ion are affected by the electric field of the ligands to different extent. This causes the splitting of *d*-orbitals into groups of different energies. The electronic transition from one group to other now takes place with absorption of energy. The energy difference is of such a magnitude that absorption takes place in the visible region and the complexed ion appears to be coloured in solution.

Explanation of the Origin of Colour in Complex Ions. The origin of colour in transition metal complexes has been explained by applying **Crystal field theory.** A fundamental postulate of this theory is that *the bonding in transition metal complexes is electrostatic.* Let us take the example of Ti^{3+} ion. The free ion contains

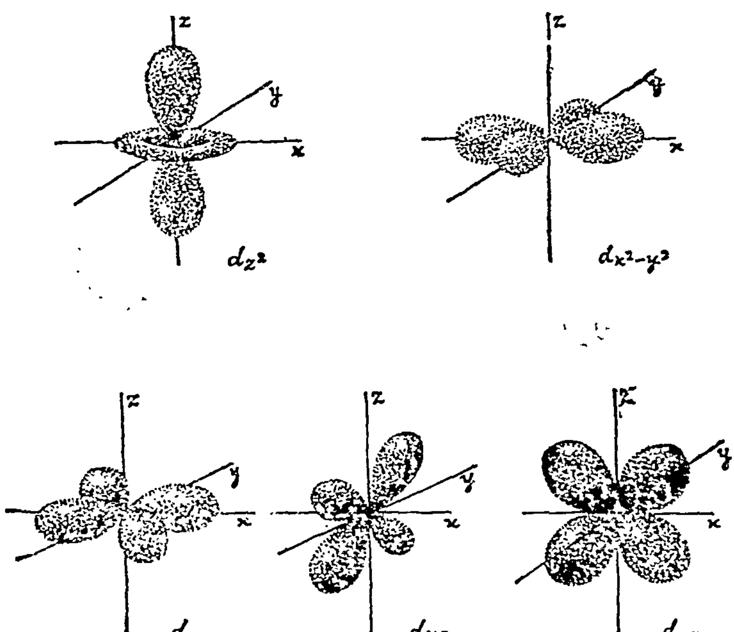


Fig. 1·9. *d*-orbitals.

only one electron in *d*-orbitals. The five *d*-orbitals are shown in Fig. 1.9, and the solitary electron spends its time equally in all the five *d*-orbitals. These orbitals fall into two groups :

(*i*) d_{z^2} and $d_{x^2-y^2}$ orbitals. have high electron probabilities along the *x*, *y* and *z* axes.

(*ii*) d_{xy}, d_{yz} and d_{zx} orbitals have high electron probabilities in the regions between the axes *x*, *y* and *z*.

As the coordination number of Ti^{3+} is 6, in aqueous solution it combines with six water molecules (ligands) octahedrally disposed along the three axes *x*, *y* and *z* as shown in Fig. 1·10. It is clear from the figure that the central metal ion will exist in an electric field due to the presence of these ligands. This field is called **ligand field.** As the (*i*) group of orbitals, *i. e.*, $d_{x^2-y^2}$ and d_{z^2} orbitals i.e., directed along the axes, they will be in close proximity to the ligands. Any electron in these orbitals will experience a strong repulsion and will therefore be raised in energy. On the other hand, the (*ii*) group of orbitals, *i. e.*, d_{xy}, d_{yz} and d_{zx} orbitals will not be in so much proximity to the ligands, as they are not directed towards the axes. Hence any electron in these orbitals will experience a relatively lesser electrostatic repulsion and will therefore be raised in energy to a lesser extent. Thus, the d-orbitals are split up into two groups by the octahedrally disposed ligands as shown in Fig. 1·11 (*b*). The (*i*) group of $d_{x^2-y^2}$ and d_{z^2} orbitals, which are raised to the higher energy level, are called **e_g orbitals.** The (*ii*) group of d_{xy}, d_{yz} and d_{zx} orbitals, which are raised comparatively at the low energy level, are called **t_{2g} orbitals.** As t_{2g} orbitals are energetically favoured the solitary *d*-electron of Ti^{3+} now spends its time preferably in these orbitals as shown in Fig. 1·11 (*b*). It is only after the absorption of energy, $\Delta = h\nu$, that the electron will be excited and raised to the higher energy level, *i.e.*, e_g orbital as shown in Fig. 1·11 (*c*). Such electronic transitions are known as **d-d transitions.** The frequency ν of

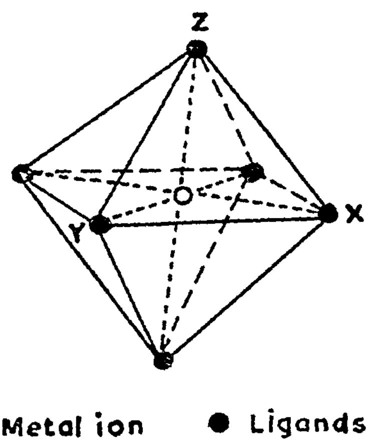


Fig. 1·10 Octahedral Disposition of Ligands around Ti^{3+}.

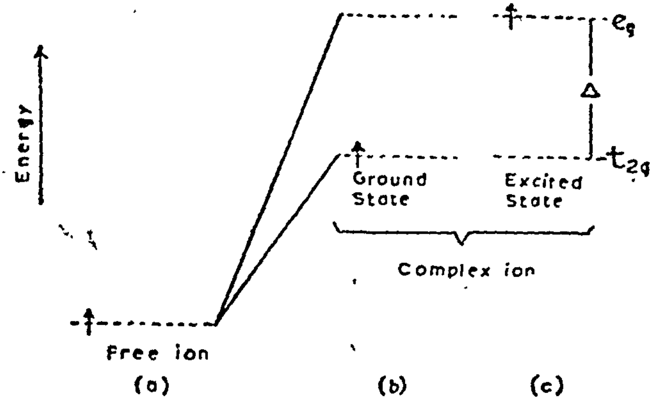


Fig. 1·11 Schematic representation of Splitting of *d* Orbitals of Free Metal Ion in an Octahedral Field.

absorption, which is equal to Δ/h, is of such magnitude that Ti^{3+} absorbs in the visible region. The absorption spectrum of $Ti(H_2O)_6^{3+}$ is shown in Fig. 1·12., in which a broad band is seen in the neighbourhood of 5000 Å. This implies that the central portion of visible spectrum is absorbed and therefore subtracted. Thus, the red and violet components remain unabsorbed imparting purple colour to the complex ion of titanium, *i.e.*, $Ti(H_2O)_6^{3+}$.

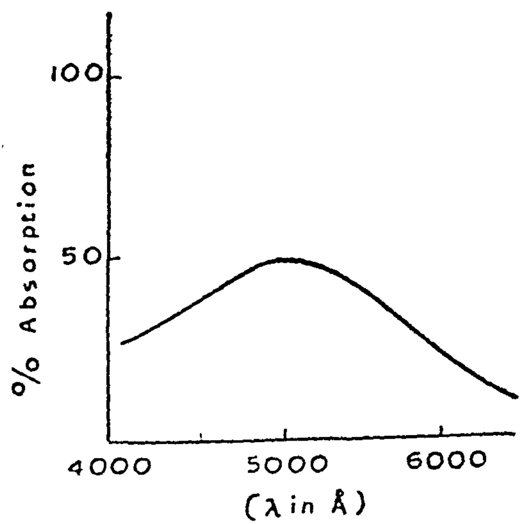


Fig. 1·12 The Absorption Spectrum of $Ti(H_2O)_6^{3+}$

Applications of Ultraviolet and Visible Spectroscopy

The literature is full of various applications of ultraviolet and visible spectroscopy in different fields of chemical interest. However, a few important applications will be given here.

(*i*) Identification and Assignment of Structure.

The absorption spectrum of an unknown compound is compared with those of a number of known compounds. If the absorption spectrum of the unknown compound tallies with a particular known compound, then the structures of the two will also be similar. The absorption spectra of synthetic (unknown) and natural (known) vitamin A_2 are shown in Fig. 1·13. The similarity between the two spectra proved helpful in the identification and assignment of structure of synthetic vitamin A_2. *The technique in which the spectrum of an unknown compound is tallied with those of known compounds, is known as* **finger printing.**

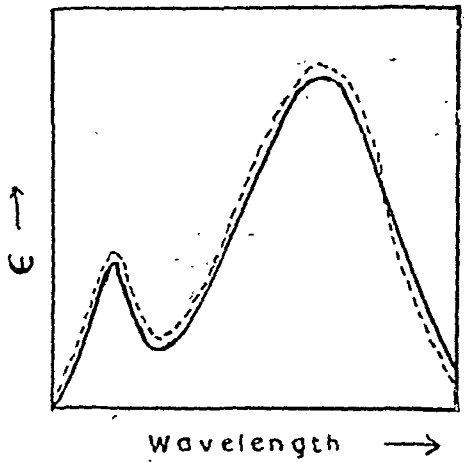


Fig 1·13 Absorption Spectrum of Vitamin A_2 in Ultraviolet Region, ...Natural product,—Synthetic Product.

(*ii*) **Quantitative Analysis.** Ultraviolet and visible spectrophotometric methods have been used to determine the unknown concentration of a compound in solution. The essential condition to develop such a method is that Beer's law, $A = \epsilon cb$, must be obeyed in the range of concentration to be used. The absorbance A is measured directly from spectrophotometer at various concentrations c of the solution. A graph is then plotted between A and c as shown in Fig. 1·14. Absorbance A' of the solution of unknown concentration is then determined by spectrophotometer and its concentration c' is then determined from the graph (Fig. 1·14). The extinction coefficient ϵ can also be evaluated from the slope of the graph.

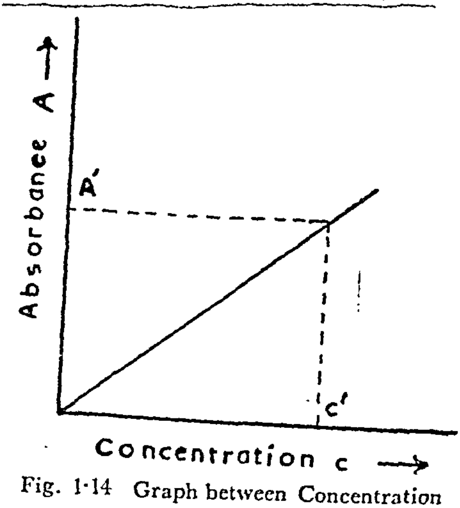


Fig. 1·14 Graph between Concentration and Absorbance.

(*iii*) **Control of Purification.** Ultraviolet and visible spectrophotometry is used for the control of purification of a

compound. If a compound is transparent in ultraviolet and visible regions, then its purification is continued until it gives a minimum value of absorbance. On the other hand, if a compound absorbs in ultraviolet and visible regions, then its purification is continued until its molar extinction coefficient ϵ attains a constant maximum value.

(*iv*) **Determination of Molecular Weight:** Let M be the molecular weight of the compound. First $E_{1cm}^{1\%}$, *i.e.*, the absorbance of 1% solution of compound in a 1 cm thick cell, is determined. In this case, the molar concentration, $c = 10/M$ mole per lit., cell thickness, $b = 1$ cm and absorbance, $A = E_{1cm}^{1\%}$. Putting these values in Beer's law equation

$$A = \epsilon cb$$

we get

$$E_{1cm}^{1\%} = \epsilon \frac{10}{M}$$

or

$$M = \frac{10\epsilon}{E_{1cm}^{1\%}} \qquad \ldots(1{\cdot}12)$$

Molecular weight M of the compound can be evaluated from Eq. (1·12).

(*v*) **Study of Kinetics.** If the λ_{max} values of reactants and products of a chemical reaction are quite different, then the change in the concentrations of reactants or products can be followed spectrophotometrically and kinetics of the reaction can be studied. Spectrophotometric methods are particularly useful when the reactions are fast and the solutions are very dilute, *e.g.*, photochemical transformation of ergosterol to vitamin D_2 is well suited for spectrophotometric method.

(*vi*) **Other Physico-chemical Studies.** Apart from these, ultraviolet and visible spectrophotometry has been very useful in other physico-chemical studies, such as determination of dissociation constants of acids and bases, heats of formation of molecular addition compounds and complexes in solution, empirical formulae of complexes in solutions etc.

INFRARED SPECTROSCOPY

Introduction.

The region from 0·8 μ to 200 μ of the electromagnetic spectrum is called **infrared region** *and the study of spectra in this region is referred to as* **infrared spectroscopy.** The following names have been given by the spectroscopists to differentiate the various regions in connection with infrared spectroscopic work.

Region	Wavelength range (μ)
1. Near infrared	0·8 to 2·5
2. Ordinary infrared	2·5 to 15
3. Far infrared	15 to 200

Thus, it is clear that near infrared region corresponds to shorter wavelength (higher frequency) as compared to far infrared region. Hence absorption of radiations by molecules in the near infrared are accompanied with higher energy than those in the far infrared region. When a molecule absorbs in the far infrared region, only the transitions in the rotational energy take place, because these transitions require least energy. The spectra produced are, therefore, called **pure rotational spectra.** When a molecule absorbs in the near or ordinary infrared region, greater energy is available and the transitions in the vibrational as well as rotational energy take place. The spectra produced are, therefore, termed as **vibrational rotational spectra.** These spectra are particularly useful for the chemists for the study of molecular structure.

Instrumentation. Infrared absorption spectra are generally obtained by placing the sample in one of the beam of double-beam spectrophotometer. The light source is Nernst glower. It is a moulded rod which contains a mixture of the oxides of rare earths heated to 1500°C. Prism or grating is used as monochromator. Cell containers and prisms are made of metal halides, such as NaCl. Thermocouple or bolometer is used as detector. The basic arrangement of various instrumental units has already been shown in Fig. 1·3.

The sample may be in the form of gas, solid, liquid or solution. It should be dry as water absorbs near 2·7μ. The solution is made in solvents like CCl_4, CS_2, and $CHCl_3$ which have few absorption in infrared region.

Basic Principles of Infrared Absorption.

A. Modes of Vibrations. The vibrational motion of atoms in a molecule can be visualized as a mechanical model consisting of a system of balls of different masses connected with springs of different tensile strengths. The balls and the springs correspond to the various atoms and chemical bond in the molecule respectively and their arrangement is in accordance with the space geometry of the molecule. If such a model is suspended and a blow is struck to it, all the balls will undergo a random vibrational motion. The atoms of a poly-atomic molecule can be thought of undergoing such vibrational chaotic motion. The complexity of this vibrational motion increases with the number of atoms in the molecule. However, a simplification is achieved by realizing that this random vibrational motion of a molecule can be resolved into a small number of **normal** or **fundamental vibrations** or **normal modes.** A **normal mode** *of a polyatomic molecule can be defined as a vibrational state in which each atom undergoes a simple harmonic motion about its equi-*

*librium position, possesses the same frequecy and moves 'in phase'**. The centre of gravity of the molecule is preserved during these vibrations so that there is no translational motion of the molecule. The number of normal modes is equal to $(3N-6)$ for non-linear and $(3N-5)$ for linear molecules, where N is the number of atoms in a polyatomic molecule. The normal modes of vibrations in a molecule are of various types. Some of the important types are categorised as follows :

- Normal
  - Stretching
    - Symmetric
    - Asymmetric
  - Bending
    - Scissoring
    - Wagging
    - Rocking
    - Twisting

Stretching or Valence bond Vibrations *are those vibrations in which the vibrating atoms move along the bond between them.* Thus, the bond length varies during these vibrations. Stretching vibrations for—CH_2—group are shown in Fig. 1·15. These vibrations are of two types :

(*a*) Symmetric and (*b*) Asymmetric

(*a*) **Symmetric Stretching** *are those vibrations in which the bonds stretch and compress simultaneously* as shown in Fig. 1·15 (*a*). The two H-atoms move towards and away from the C-atom simultaneously.

(*b*) **Asymmetric stretching** *are those vibrations in which the atoms do not move in unison, i.e.*, when one H-atom approaches the C-atom, the other H-atom moves away from the C-atom as shown in Fig. 1·15 (*b*).

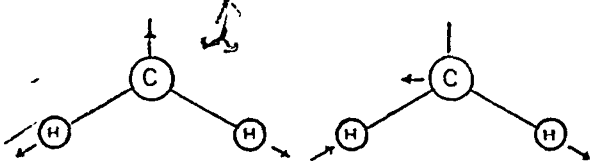


Fig. 1·15. Stretching Vibrations for—CH_2—group
(*a*) Symmetric (*b*) Asymmetric

Bending or Deformation Vibrations. When a three atom system is a part of a big molecule, then bending vibrations may occur. *Those vibrations in which the atoms or the group as a whole oscillates perpendicular to the bond axis are called* **bending or deformation vibrations.** Four important types of bending vibrations are :

**In phase.* If all nuclei pass through their mean positions and reach their turning point simultaneously during vibrations, then they are said to be 'in phase'.

(*a*) **Rocking** *vibrations are those in which the vibrating group swings back and forth in the plane of the molecule* as shown in Fig. 1·16 (*a*).

(*b*) **Wagging** *vibrations are those in which the vibrating group swings back and forth out of the plane of molecule* as shown in Fig. 1·16 (*b*).

(*c*) **Twisting** *vibrations are those in which the vibrating group rotates about the chemical bond by which it is attached to the rest of the molecule* as shown in Fig. 1·16 (*c*).

(*d*) **Scissoring** *vibrations are those in which two atoms attached to a central atom move away from and towards each other* as shown in Fig. 1·16 (*d*).

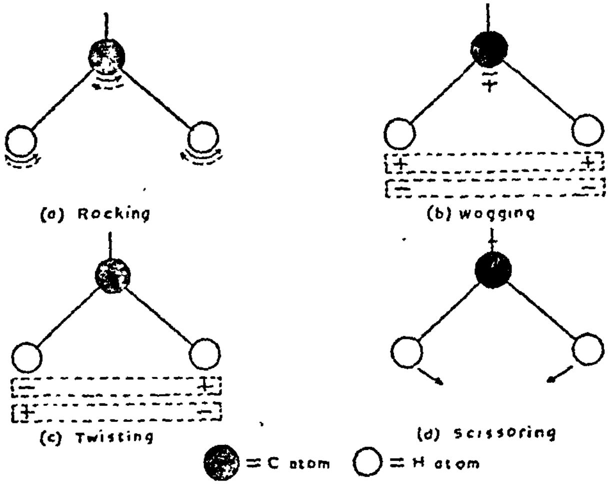


Fig. 1·16 Bending Vibrations of CH_2 group. + and—refer to Vibrations Perpendicular to the Page.

B. Conditions for Absorption of Infrared Radiations. According to classical electrodynamics, there are two requirements which must be fulfilled in order that the molecule absorbs radiations :

1. The vibrational frequency of the molecule must be the same as the frequency of radiation. As we have seen, an electromagnetic radiation has its electrical and magnetic components. The molecule also possesses an electric field. If the electric field of the molecule vibrates at the same frequency as that of the electromagnetic radiation, then energy is absorbed by the molecule from radiation. Following analogy of tuning fork experiment may be helpful to understand this process :

Experiment. Fix three tuning forks P, Q, and R a few centimeters apart on a table. Let the frequencies of P and Q be the same, but that of R be different. Now strike P so that it starts vibrating. It is seen that Q also starts vibrating, but R remains motionless. This happens because the frequencies of vibrations of P and Q are equal, so Q absorbs energy produced by P. R does not absorb energy and remains motionless because its frequency is different.

2. *There must be a change in the dipole moment of the molecule as a result of vibration.* This change in dipole moment may be in magnitude or direction or both. Dipole moment is determined by the positions of the centres of gravity of positive and negative charges. During a vibrational mode, the positions of the charges change. This may result in the change of dipole moment. If the values of dipole moments in the extreme positions of vibrations differ, a periodically changing electric field will occur around a molecule. Now if the molecule vibrates at the same frequency as that of incoming radiation (in fulfilment of condition 1), then the frequency of this changing electric field will be the same as that of the incoming radiation. Consequently, absorption of radiation will take place.

The analogy of tuning fork experiment is again helpful. Just as the tuning fork Q requires air as a carrier of energy from P, in the same way, a molecule must also possess something to *couple* with the energy from radiation. Dipole moment acts as a coupler.

C. Position of Absorption Bands. The position of absorption bands can be given by the classical theory of harmonic oscillators. Consider the simplest case of a vibrating diatomic molecule AB. The two atoms in the molecule can be thought of as point masses m_A and m_B connected by a spring representing the bond strength. If the two atoms A and B execute simple harmonic motions about an equilibrium point, then the frequency $\bar{\nu}$ (in wave number) can be given by

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \ldots(1\cdot13)$$

where k is the force constant, *i. e.*, restoring force per unit displacement in dynes/cm, μ is the reduced mass (in gm) given by

$$\mu = \frac{m_A\ m_B}{m_A + m_B}$$

and c is the velocity of light in cm/sec.

We know that $\bar{\nu}$ also represents the position of absorption. In order to evaluate it from Eq. (1.13), it is nesessary to obtain the value of force constant. For this purpose Gordy's empirical relation can be used as given below :

$$k = aN\left(\frac{x_A\, x_B}{d^2}\right) + b \qquad \ldots(1\cdot14)$$

where N is the bond order*, x_A and x_B are the electronegativities of atoms A and B respectively on Pauling's scale and d is the internuclear distance in Angstroms. a and b are constants whose values are 1·67 and 0.30 respectively for stable molecules having normal covalencies.

***Bond order.** The degree of multiplicity of a chemical bond is generally described in terms of bond order. It is the effective number of covalent or ionic bonds between two atoms.

Absorption of Common Functional Groups.

Eq. (1·13) can be used to evaluate $\bar{\nu}$ for a particular bond provided k for that bond is known. For illustration, the following examples may be given.

Example. 1·2. *Calculate the fundamental frequency expected for C—H bond in methane. Force constant and reduced mass may be taken as 5×10^5 dynes cm^{-1} and $1{\cdot}672\times10^{-24}$ gm.*

Solution.

We know that $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

Here $c=3\times10^{10}$ cm sec^{-1}, $k=5\times10^5$ dynes cm^{-1}, and $\mu=1{\cdot}672\times10^{-24}$ gm.

$$\therefore \quad \bar{\nu} = \frac{1}{2\times3{\cdot}14\times3\times10^{10}}\sqrt{\frac{5\times10^5}{1{\cdot}672\times10^{-24}}}$$

$$=1902 \text{ cm}^{-1}$$

Example 1·3 *Calculate the fundamental frequency in the infrared absorption spectrum for C—O stretching vibrations ($k=5\times10^5$ dynes cm^{-1}).*

Solution.

We know that, $\mu_{co} = \frac{m_c\, m_o}{m_c+m_o}$

Here $m_c = \frac{12}{6{\cdot}023\times10^{23}}$, and $m_o = \frac{16}{6{\cdot}023\times10^{23}}$

$$\therefore \quad \mu_{co} = \frac{\frac{12\times16}{(6{\cdot}023\times10^{23})^2}}{\frac{(12+16)}{6{\cdot}023\times10^{23}}} = \frac{12\times16}{28}\times\frac{1}{6{\cdot}023\times10^{23}}$$

Again we know that

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Here $c=3\times10^{10}$ cm sec^{-1}, $k=5\times10^5$ dynes cm^{-1}

$$\therefore \quad \bar{\nu} = \frac{1}{2\times3{\cdot}1416\times3\times10^{10}}\sqrt{\frac{(5\times10^5)(28)(6{\cdot}023\times10^{23})}{(12)(16)}}$$

$$=1110 \text{ cm}^{-1}.$$

From example 1·2, the fundamental frequency of vibration for C—H bond in methane comes to be 2902 cm^{-1}. Hence the molecule must absorb the radiation of this frequency. Actually, there is a strong band at 2915 cm^{-1} in the infrared absorption spectrum of methane. In the same way, $\bar{\nu}$ for C=O bond in acetone as calculated from Eq. (1·13) is 1730 cm^{-1}. Actually, acetone is

found to absorb strongly at 1744 cm^{-1} in the infrared spectrum. These and similar other results prove the validity of treating the atoms in the molecule as harmonic oscillators.

It is clear from Eq. (1.13) that fundamental frequency $\bar{\nu}$ depends upon.

(*i*) force constant of the bond, and

(*ii*) reduced mass.

As different functional groups in organic compounds have the characteristic values of force constants and reduced masses, they will absorb at characteristic frequencies. Use of Eq. (1·13) for determining the frequencies of normal vibrations for various possible combinations of atoms in a molecule shows that they fall in the region 2·5—50μ, which is ordinary infrared region. Thus, the common functional groups of organic compounds absorb in the infrared region with characteristic frequencies. The characteristic frequencies of some simple and common functional groups are given in Table 1·6.

C=O Vibrations in ketones, carboxylic acids, amides and etsers—Ketones, carboxylic acids, amides and esters show a strong C=O stretching absorption band in the region 5·35-6·50μ This band can be recognized easily due to its relatively constant position, high intensity and freedom from interfering bands . The absorption frequency of saturated aliphatic ketone is normally 5·83μ. The C=O stretching bands of carboxylic acids are more intense than those of the ketonic C=O. The saturated aliphatic acids absorb, near 5·68μ and 5·83μ in monomer and dimer forms respectively. The C=O absorption band of saturated aliphatic esters is in the region 5·71-5·76μ. The absorption band of primary amides, except acetamide, occurs at 5 90μ. Secondary amides absorb near 6·10μ in the solid state. For tertiary amide the absorption occurs in the range 5·95-6·13μ.

O—H Vibration in alcohols, water and Phenols. The free O—H group of alcohols and phenols absorbs in the region 2·74-2·79μ. With increase in the concentration intermolecular hydrogen bonding increases and additional bonds appear at 2·82-3·13μ. Alcohols and phenols absorb in the region 13·0-15·4μ due to —OH bending vibrations. Water absorbs in the region 2·66-2·74μ and near 6·27μ due to —O—H stretching and bending vibrations.

C—H Vibration in alkanes, benzene and simple aromatic substituted compounds. Alkanes generally absorb in the region 3·3-3·5μ. The positions of C—H stretching vibrations are one of the most stable.

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Again we know that

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$$\therefore \quad \bar{\nu} = \frac{1}{2\times3\cdot1416\times3\times10^{10}}\sqrt{\frac{(5\times10^5)(28)(6\cdot023\times10^{23})}{(12)(16)}}$$

$$\approx 1110 \text{ cm}^{-1}.$$

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C—H Vibration in alkanes, benzene and simple aromatic substituted compounds. Alkanes generally absorb in the region 3·3–3·5μ. The positions of C—H stretching vibrations are one of the most stable.

Table 1·6
Characteristic Infrared Absorption of Common Functional Groups

Group Vibrations with Parent Compound	*Wavelength range* (μ)	*Frequency range* (cm^{-1})
(*i*) **C=O Stretching**		
Ketones saturated	5·80—5·87	1725—1705
Ketones unsaturated	5·94—6·01	1685—1665
Aryl ketones	5·88—5·95	1700—1680
Saturated aliphatic carboxylic acids	5·80—5·88	1725—1700
Arly carboxylic acids	5·88—5·95	1700—1680
Primary amide (in dil. soln.)	∽5·95†	∽1690
Secondary amide (in dil. soln.)	5·88—5·99	1700—1670
Tertiary amide	5·99—6·14	1670—1630
Saturated acyclic ester	5·71—5·76	1750—1735
(*ii*) **O—H Sutretching**		
(*a*) *In alcohols and phenols*		
Free O—H	2·74—2·79	3650—3590
Intermolecularly hydrogen bonded	2·82—3·13	3550—3200
(*b*) *Water*	2·66—2·74	3780—3650
(*iii*) **O—H Bending**		
Primary alcohols	∽9·5	∽1050
Secondary alcohols	∽9·1	∽1100
Tertiary alcohols	∽8·7	∽1150
Phenols	∽8·3	∽1200
Water	∽6·27	∽1600
(*iv*) **C—H Stretching**		
Alkanes	3·38—3·51	2962—2853
Alkenes	3·23—3·32	3095—3010
Aromatic	∽3·30	∽3030
(*v*) **C—H Bending**		
Alkane	∽7·46	∽1340
Alkene (monosubstituted)	10·05—10·15	995—985
Aromatic substituted*		
5 adjacent H-atoms	∽13·3 and ∽14.3	∽750 and ∽700
4 ,, ,,	∽13·3	∽750
3 ,, ,,	∽12·8	∽780
2 ,, ,,	∽12·0	∽830
1 ,, ,,	∽11·3	∽880
(*vi*) **N—H Stretching**		
Primary amine	∽2·86 & 2·94	3500 & 3400
Secondary amine	2·86—3·02	3500—3310
(*vii*) **N—H Bending**		
Primary amine	6·06—6·29	1650—1590
Secondary amine	6.06—6·45	1650—1550
(*viii*) **C—X Stretching**		
In Halogen Compounds		
C—F	7·1—10·0	1400—1000
C—Cl	12·5—16·6	800—600
C—Br	16·6—20·0	600—500
C—I	∽20	∽500

*Substituted benzenes also show weak bands in the region 5·0—6·0μ (2000—1670cm^{-1}).

†∽=approximately.

Aromatic C—H stretching band appears between 3·23–3·33μ. The absorption of substituted benzenes are shown in table 1·6. The position of absorption is characteristic of the number of adjacent atoms in the ring. These bands are generally intense. The position of absorption shown in table are generally reliable for alkyl substituted benzenes.

N—H Vibrations in amines. Primary amines show two weak bands near 2·86μ and 2 94μ. Secondary amines display a weak band in the region 2·98-3·02μ Hydrogen bonding shifts these bands to higher wave-lengths. The N—H bending vibration of primary amines is seen in the region 6·06–6·33μ. The band shifts to the lower wave-lengths when the compound is associated.

C—X stretching vibration in halogen compounds Aliphatic C—Cl broad absorption band is seen in the region 11·76–18·18μ. If many chlorine atoms are linked to one carbon atom, band becomes more intense and is found at lower wave-length end of the assigned range. Compounds containing fluorine strongly absorb in the range 7·15–13·70μ due to C—F stretching vibrations. Brominated and iodo-compounds absorb in the regions 14·5–19·4μ and 16·6–20·0μ respectively.

Applications of Infrared Spectroscopy

There are many applications of infrared spectroscopy in various fields of chemical interest. However, a few important ones are described here.

1. Determination of Force Constant of a Bond. It is of special interest to a chemist to find out the force constant of a bond, because it is a measure of the strength of the bond as is clear from the Table 1·7. We know that the frequency of absorption $\bar{\nu}$ is related to force constant k by the relation

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

or
$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu \qquad ...(1·15)$$

$\bar{\nu}$ is measured from infrared spectroscopy and k can be calculated for a bond.

Example 1·4 *The absorption band of HCl is centred at 2890 cm^{-1} in infrared region. Calculate the force costant for the H—Cl bond [μ=1·627 × 10^{-24} gm].*

Solution We know that

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu.$$

Here $c = 3\times10^{10}$ cm/sec' $\bar{\nu}$ = 2890 cm^{-1}, $\mu = 1·627\times10^{-24}$ gm.

$\therefore$ $k = 4(3·14)^2(3\times10^{10})^2(2890)^2(1·627\times10^{-24})$
$= 4·84\times10^5$ dynes cm^{-1}

Table 1·7 gives the values of force constants and bond energy for some diatomic molecules which absorb in infrared region. It is apparent from the table that the value of k determines the relative strengths of the bonds.

Table 1·7

Force Constants for Some Bonds

Bond	*Infrared λ_{max} (μ)*	*Force constant (dynes/cm) $\times 10^5$*	*Bond Energy (Kcal/mole)*
H—F	3·44	9 7	135
H—Cl	3·47	4·8	102
H—Br	3·77	4·1	87
H—I	4·48	3·2	71

2. **Structure Elucidation and Identification of a Compound.** We have already seen that different functional groups in a polyatomic molecule absorb at characteristic frequencies. This phenomenon has been helpful in the elucidation of structure of organic compounds. When the infrared spectrum of a compound is obtained, then the presence and absence of certain functional groups in the compound is known. For example, if the spectrum of a compound shows a strong absorption at 5·82 μ, then a carbonyl group should be present in it. If the spectrum contains no absorption in the region 5·4—6·3 μ, then it is certain that no carbonyl group is present in the compound. When the presence of different functional groups in the compound is thus established, then the structure can be elucidated with the help of other available data.

The most useful function of infrared spectroscopy is the identification of an unknown sample by matching its spectrum with that of a known compound. This is known as **fingerprint technique** as already described.

3. **Determination of Purity.** We know that each particular compound has a characteristic infrared spectrum. If impurities are present in it, then extra absorption bands will appear in the spectrum and some parts of the spectrum will not be so sharp. Thus, infrared spectrum can be used to determine the purity of a compound.

4. **Study of Reaction Kinetics.** In a chemical reaction one expects the breaking of some bonds and producing new bonds. Accordingly, certain bands in the infrared spectrum would disappear and new bands will appear in the course of time. Thus, the progress of many organic reactions can be followed by withdrawing aliquots at different intervals and examining their infrared spectra.

TEST YOUR KNOWLEDGE

1. Give a term for each of the following :

(*i*) Study of absorption and emission of electromagnetic radiations by matter.

(*ii*) Phenomenon in which white light is separated into its coloured components.

(*iii*) The number of wavelengths per cm.

(*iv*) The distance travelled by a wave during a complete cycle.

(*v*) Extinction due to 1 cm thick layer of solution whose molar concentration is unity.

(*vi*) The wavelength corresponding to maximum absorption.

(*vii*) Shift of absorption band towards shorter wavelengths.

(*viii*) The effect in which a substituent causes to decrease the intensity of an absorption band.

(*ix*) Vibrations in which atoms move along the bond between them.

(*x*) Restoring force per unit displacement.

2. Fill in the blanks with appropriate words :

(*i*) When white light is passed through a prism. the band of colours produced is called......

(*ii*) The complete optical system for producing and viewing a spectrum is known as optical......

(*iii*) The instrument which makes the photographic record of the spectrum is known as......

(*iv*) The number of wavelength passing through any point per second is known as......

(*v*) An ordered arrangement of.........according to wavelength is called electromagnetic spectrum.

(*vi*) The spectra of......is called band spectra.

(*vii*) The complex structure of molecular spectra consists of a greater number of closely packed......

(*viii*) Rotational spectra are produced due to the transitions in......energy of molecules.

(*ix*) The fraction of light......is proportional to the number of solute molecules in the path travelled.

(*x*) The vibrational motion of a polyatomic molecule can be res...... to a small number of......vibrations.

(*xi*) The fundamental frequency of a diatomic molecule depe...... and......

(*xii*) ......is an isolated functional group not in conjugatio... colour to a compound.

3. **Complete the following :—**

(*i*) 1 micron (μ) $=$......cm

(*vi*) $...... = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

(*ii*) $\nu = .../c$

(*vii*) $\mu = \frac{......}{m_A + m_B}$

(*iii*) $A = \log_{10} \frac{...}{I}$

(*viii*) $k = aN\left(\frac{...}{d^2}\right) + b$

(*iv*) $T = -\epsilon c...$

(*ix*) $... = 4\pi^2 c^2 \bar{\nu}^2 \mu$

(*v*) $M = \frac{10\epsilon}{......}$

(*x*) 1 Angstrom = ...$m\mu$

KEY

1. (*i*) Spectroscopy (*ii*) Dispersion (*iii*) Wave number (*iv*) Wavelength (*v*) Molar extinction coefficient (*vi*) λ_{max} (*vii*) Hypsochromic shift (*viii*) Hypochromic effect (*ix*) Stretching vibrations (*x*) Force constant.

2. (*i*) Spectrum (ii) Spectroscope (*iii*) Spectrograph (*iv*) Frequency (*v*) Radiations (*vi*) molecules (*vii*) lines (*viii*) rotational (*ix*) absorbed (*x*) normal or fundamental (*xi*) force constant, reduced mass (*xii*) chromophore.

3. (*i*) 10^{-4} (*ii*) ν (*iii*) I_0 (*iv*) b (*v*) $E^{1\%}_{1cm}$ (*vi*) $\bar{\nu}$ (*vii*) $m_A m_B$ (*viii*) X_A X_B (*ix*) k (*x*) 10^{-1}

QUESTIONS

1. What is an optical spectroscope ? Describe its various parts with an optical diagram. What modifications are made in a spectroscope for the construction of (*a*) Spectrometer (*b*) Spectrograph, and (*c*) Spectrophotometer ?

2. What is the nature of electromagnetic radiation ? What is the wavelength range of following radiations in Angstrom units ?

   (*a*) Ultraviolet rays (*b*) Visible light (*c*) Infrared rays.

3. What do you understand by emission and absorption spectra ? Describe their classification.

4. Give the basic arrangement of various instrumental units in an absorption spectrometer diagrammatically and describe each unit.

5. What are band spectra ? Describe their origin in terms of electronic, vibrational, and rotational transitions. How will you classify band spectra ?

6. What do you understand by ultraviolet and visible spectroscopy ? Describe its applications.

7. State Beer-Lambert's law. Explain the terms : absorbance, transmittance, and molar extinction coefficient. What are the limitations of Beer-Lambert's law ? Give the various factors which cause deviation from this law.

8. Write short notes on :

   (*i*) Chromophores (*ii*) Auxochromes (*iii*) Effect of substituents on electronic bands, (*iv*) Absorption of common functional groups.

9. Discuss the origin of electronic absorption bands. What are K-band, B-band, and R-band ?

10. Discuss the origin of colour in transition metal ions with a suitable example.

11. What is infrared spectroscopy ? Describe its important applications.

12. What do you understand by a normal mode of vibration. Describe the various types of normal modes in a polyatomic molecule with diagrams.

13. What are the conditions for the absorption of infrared radiations? How will you determine the position of an absorption band in wave numbers?

14. Explain the terms :
(*i*) Wave number (*ii*) Continuous spectra (*iii*) Sample cell (*iv*) Absorption spectrum (*v*) Vibrational rotational spectra (*vi*) Extinction (*vii*) π—electrons (*viii*) Bathochromic shift (*ix*) Hyperchromic effect (*x*) Ligands (*xi*) d—d transition (*xii*) Finger printing (*xiii*) Bending vibrations (*xiv*) Bond order (*xv*) Reduced mass.

15. An absorption band occurs at 3·45 μ. What is its frequency in wave numbers? Calculate the energy associated with band in ergs/mole.

$$(1\ \text{cm}^{-1} = 1{\cdot}985 \times 10^{-16}\ \text{ergs/molecule})$$

[Ans. 2898 cm^{-1}, $3{\cdot}46 \times 10^{11}$ ergs mole]

16. A monochromatic light was passed through a 0·01 M solution of a substance placed in a 5 cm thick cell. The intensity of transmitted light was found to be 0·245 of the incident light. Calculate the molar extinction coefficient of the substance.

[Ans. 12·2]

17. There is an intense band at 2144 cm^{-1} in the infrared spectrum of CO. Calculate the force constant.

[Ans. 18.5×10^5 dynes/cm]

18. Calculate the fundamental frequency in the infrared absorption spectrum for C—C *stretching* vibrations ($k = 4{\cdot}5 \times 10^5$ dynes/cm).

[Ans. 1122 cm^{-1}]

19. Hydrogen bromide has a vibrational frequency of $7{\cdot}96 \times 10^{13}$ cycles/sec. Calculate the force constant for the H—Br bond.

[Ans. $4{\cdot}1 \times 10^5$ dynes *per cm*]

20. How many normal modes of vibrations are there in HCN molecule? *Explain* these normal modes with diagrams.

2

The Crystalline State

Introduction.

Ancient Greeks noted that the mineral quartz usually occurs in the form of characteristic shape bounded by flat surfaces. From the transparency of mineral they thought that the freezing of water under intense cold has resulted in the formation of quartz. Hence the name *krustallos*, which means *clear ice*, was given to it. Later on the term *krustallos* was extended to all substances which had such characteristic forms bounded by flat surface. It is due to the work of Steno, Lomonosov and Hauy that the study of crystals evolved from mere speculation. Hauy argued that crystals are made of tiny *bricks* of minerals. Different arrangement of bricks gives different forms of crystals. Hauy's notion of the arrangement of bricks of minerals has now been replaced by that of arrangement of atoms or molecules or ions. Thus, chemical constitution is the deciding factor for the crystalline form. Fyodorov was able to tell the chemical composition of many substances by the study of their crystalline forms.

The science which deals with the study of the growth, external form, internal structure and physical properties of crystals is known as **crystallography**. *A body bounded by surfaces, usually flat, arranged on a definite plan which is an expression of the internal arrangement of particles* (*atoms, molecules* or *ions*) *is known as a* **crystal.** From the definition of crystal it is clear that the internal arrangement is of basic importance. We can construct a model of crystal with glass or wood. It will not be called a crystal because it lacks the fundamental property of the internal arrangement of particles on a definite plan.

Crystalline and Amorphous Substances.

Crystalline *substances are those solids which exist as crystals.* These crystals may be big or small. Some crystals are so tiny that their crystalline shape can be visible under microscope only. Apart from these, *there are many substances which lack the crystalline shape as well as the definite plan on which their internal*

arrangement is based; such substances are called **amorphous.** Glass, plastic, pitch, and sealing wax are examples of amorphous substances. The term 'amorphous' has been taken from Greek, which means 'shapeless'. The particles in the amorphous substance are arranged at random in the same way as in liquids. Hence these substances are considered as supercooled liquids. A crystalline substance possesses a *sharp melting point*, while an amorphous substance does not have any sharp melting point. Actually amorphous substances are intermediate between solids and liquids. X-ray examination has shown that there is only partial regularity in the internal arrangement of particles of which the amorphous substance is constituted. Hence *crystalline solids are true solids* in the strict sense.

An important feature to differentiate the crystalline and amorphous substances is the nature of their cooling curves as shown in

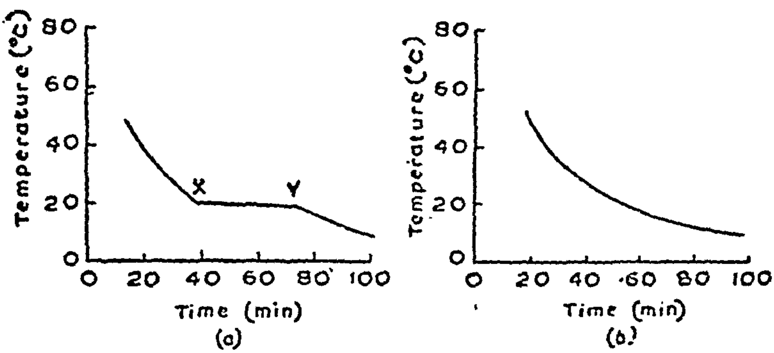


Fig. 2·1. Cooling curves for
(*a*) Crystalline (b) Amorphous substances.

Fig. 2·1. The cooling curve for a crystalline substance is discontinuous having breaks at X and Y, as shown in Fig. 2·1 (*a*). In contrast to it the cooling curve for an amorphous substance is continuous as shown in Fig. 2·1 (*b*). The breaks at X and Y in the cooling curve of crystalline substance show the beginning and end of crystallization. The temperature remains almost constant during crystallization. This is due to the fact that crystallization is accompanied by liberation of heat. This liberated energy compensates for the loss of heat in cooling and keeps the temperature constant. Since crystallization does not occur in the cooling of an amorphous substance, the curve remains continuous throughout.

To summarize, the crystalline and amorphous substances in the aspects as shown in Table 2·1.

Table 2·1
Differentiation between Crystalline and Amorphous Substances

S. No.	*Crystalline Substances*	*Amorphous Substances*
1.	The internal arrangement of particles is regular.	The internal arrangement of particles is irregular.
2.	There is regularity in the external form, when crystals are formed.	There is no regularity in the external form, when amorphous solids are formed.
3.	There is a sharp melting point.	There is no sharp melting point.
4.	The cooling curve is discontinuous.	The cooling curve is continuous.
5.	Crystalline substances are regarded as 'true solids' formed by the process of crystallization.	Amorphous substances are regarded as 'super cooled' liquids or as intermediate between solids and liquids.
6.	All crystalline substances, except those of cubic system, are anisotropic *i.e.*, their physical properties depend upon the direction of measurement.	All amorphous substances are isotropic, *i.e.*, their physical properties are the same in all directions.

Isotropic and Anisotropic Substances.

A study of physical properties of amorphous substances in different directions reveals that they have the same value of any physical property like thermal or electrical conductivity, hardness, refractive index, etc., in all directions of measurement. Such substances are called **isotropic.** As for example, the velocity of light and hence the refractive index in glass is the same, no matter in which direction it is measured. Hence glass is said to be isotropic. All amorphous substances and the crystals of cubic system are isotropic. Thus, **isotropic substances** may be defined as *those substances which give the same value of any physical property in all directions.*

All crystalline substances, except those of cubic system, give different values of a physical property in different directions of measurement. Such substances are called **anisotropic.** For example, the velocity of light and hence the refractive index in a crystal of Iceland Spar is not the same in all directions. Hence Iceland Spar is anisotropic. Thus, **anisotropic substances** *may be defined as those substances which do not give the same value of any physical property in different directions.*

Isotropic substances may be said to exhibit **isotropy**, *whereas anisotropic substances may be said to exhibit* **anisotropy**. Anisotropy is a strong evidence for the ordered arrangement of particles in crystalline substances. This can be understood with the help of a two-dimensional regular arrangement of two types of particles as shown in Fig. 2·2. It can be seen that the properties measured in the direction *XY* will be different than those measured in the direction *PQ*. It is due to the fact that each row is made up of only one type of particles in the direction *XY*, but in the direction *PQ* each row is made up of both types of particles alternately arranged. In the case of amorphous substances, the particles are arranged at random, so all directions are similar. Thus, the physical properties in amorphous substances are alike in all directions. Crystals of cubic system are exceptionally isotropic because there is a high degree of regularity in the arrangement of constituent particles in them.

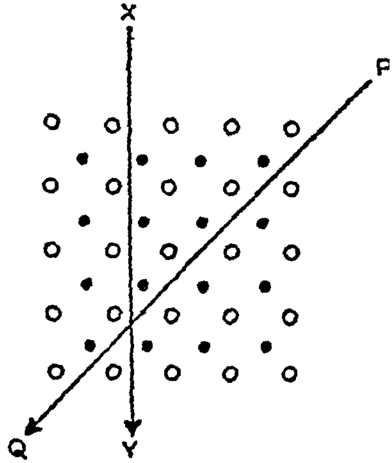


Fig. 2·2. Anisotropic behaviour of crystalline substances.

CHARACTERISTICS OF CRYSTALS

Faces. *Faces are surfaces by which the crystal is bounded.* Faces are generally flat, but sometimes they are curved also as in a specimen of diamond. Faces are of two kinds, like and unlike.

Edges. An edge is formed by the intersection of two adjacent faces.

Interfacial Angle. *Interfacial angle is the angle between the perpendiculars to the two intersecting faces.* Thus the interfacial angle between two faces F and F′ is A as shown in Fig. 2·3. Interfacial angles are measured with the instrument called **goniometer.**

Solid Angle. *A solid angle is formed by the intersection of three or more faces.*

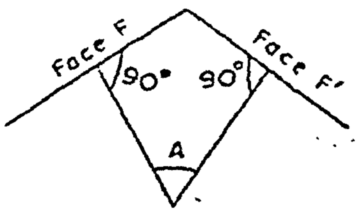


Fig. 2·3. The Interfacial Angle.

Form. Inspection of crystals shows that there are a number of like faces present in it. *Each set of like faces in a crystal is called a* **form.** *A crystal made entirely of like faces is called a* **simple form.**

Such a set of faces is called a **zone.** Each zone forms a complete belt around the crystal. *An axis through the centre of crystal and parallel to the edges of a zone is termed as* **zone axis.**

The relationship between faces, edges and solid angles may be given as

$$f + c = e + 2$$

where f, c and e are the number of faces, solid angles and edges respectively.

Symmetry. It is an important characteristic of a crystal. *A peculiar regularity observed in the arrangement of objects or their parts on a plane and in space is called* **symmetry.** Alternatively, an object has symmetry if some operation is carried out on it which converts it into itself. Such an operation is called **symmetry operation.**

Symmetry is exhibited by crystals in quite a number of different forms. It is this characteristic which forms a basis for classification of crystals.

Elements of Symmetry.

The geometrical expressions of symmetry operations are termed as **elements of symmetry.** There are several types of elements of symmetry. Three important types will be discussed here as given below :

1. **Plane of symmetry** *is an imaginary plane which divides the crystal into two parts such that one half is the mirror image of the other.* In other words, a plane of symmetry divides the crystal into two identical and similarly placed halves. Any line drawn perpendicular to this plane intersects the surfaces of crystal at equal dis-

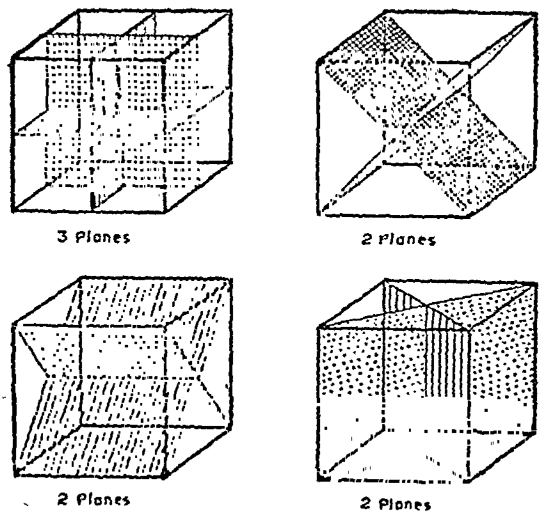


Fig. 2·4. Planes of symmetry in a cube.

tances on either side. The plane of symmetry can be illustrated by taking the example of a cube. Fig. 2·4 shows dissected planes in a cube. In all, there are 9 planes of symmetry in a cube. The inspection of a brick shows that there are only 3 planes of symmetry in it.

2. **Axis of Symmetry** *is an axis about which if the crystal is rotated, then it occupies the same position in space more than once in a rotation through 360°.* There are various types of axes of symmetry depending upon the degree of symmetry of a crystal. Following types of axes of symmetry are found in a cube :

(*a*) **Axis of Two-fold Symmetry** or **Diad** *is that axis about which if a crystal is rotated, then it occupies the same position two times in a complete rotation.* An axis of two-fold symmetry for a cube is shown in Fig. 2·5 (*a*). This axis intersects at the middle points

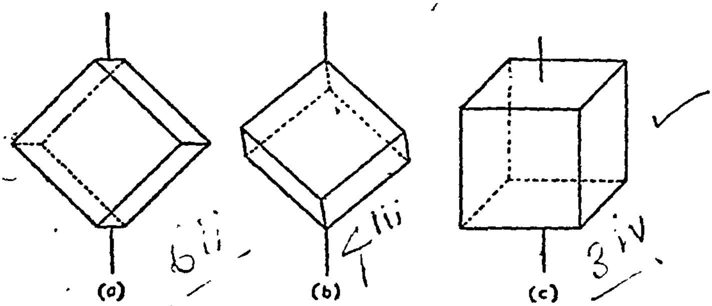


Fig. 2·5. Axes of symmetry in a cube.

of the two opposite edges of the cube. As there are 12 edges in a cube, there will be in all 6 axes of two-fold symmetry.

(*b*) **Axis of three-fold Symmetry** or **Triad** *is that axis about which if a crystal is rotated, then it occupies the same position three times in a complete rotation.* Fig. 2·5 (*b*) shows an axis of three-fold symmetry for a cube. This axis intersects at the two opposite solid angles of a cube. As there are eight solid angles in a cube, there will be in all four axes of three-fold symmetry.

(c) **Axis of four-fold Symmetry** or **Tetrad** *is that axis about which if a crystal is rotated, then it occupies the same position four times in a complete rotation.* Fig. 2·5 (*c*) shows an axis of four-fold symmetry for a cube. It intersects at the middle points of the two opposite faces of a cube. As there are six faces in a cube, there will be in all 3 axes of four-fold symmetry.

Thus, there are 13 axes of symmetry in a cube. Examination of a brick shows that there are only 3 axes of two-fold symmetry in it.

3. **Centre of Symmetry** *is an imaginary point inside the crystal such that any straight line drawn through it will intersect the faces, edges or solid angles of the crystal at equal distances on opposite sides.* Alternatively, a centre of symmetry is a centre inside the crystal around which like faces, edges and solid angles are arranged in pairs on opposite sides at equal distances. A crystal may have one or more than one planes or axes of symmetry, but it cannot possess more than one centre of symmetry. A crystal may have either one or no centre of symmetry. A cube possesses a centre of symmetry as shown in Fig. 2·6. A brick also possesses a centre of symmetry.

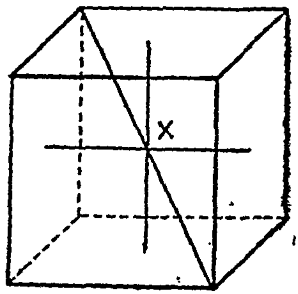


Fig. 2·6. Centre of Symmetry X in a cube.

Crystallographic Axes.

It is a usual practice in solid geometry that *the position of a plane in space is shown by the intercepts that it makes on three given lines called* **axes.** The same procedure is used in crystallography and the axes are termed as crystallographic axes. Thus, *the position of the face of a crystal in space is given by the intercepts that the face makes with the given lines called* **crystallographic axes.** The axes of symmetry, if present in a suitable number, are generally chosen as crystallographic axes. *The crystallographic axes intersect at a point called* **origin.** Certain conventions are used in the nomenclature of crystallographic axes and the angles between them as shown in Fig. 2·7. The vertical axis is called *c*. The axis running from right to left side is called *b* and that running from front to back side is called *a*. One end of each axis is positive, while the other is negative as shown in Fig. 2·7. The angle between *a* and *b* axes is called γ (gamma), that between *b* and *c* axes is called α (alpha), and that between *c* and *a* axes is called β (beta).

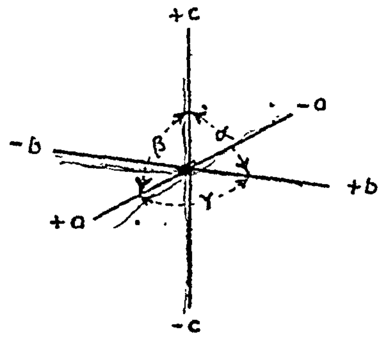


Fig. 2·7. Axial Conventions

CRYSTALLOGRAPHIC DESIGNATIONS

A concise method of showing the relation of any crystal face to the crystallographic axes is termed as **crystallographic designation.** There are a number of systems of crystallographic designations used by Miller, Weiss, Levy, Naumann, and Goldschmidt. Out of these the two chief systems oftenly used are as given below :

5. **Parameter System of Weiss.** The ratios of the distances from the origin at which a face intersects the crystallographic axes are called the *parameters* of the crystal face.

For example, ABC is the face of a crystal which intersects the crystallographic axes *a*, *b* and *c* at the distance OA, OB, and OC respectively from the origin O. The parameter of the face ABC are

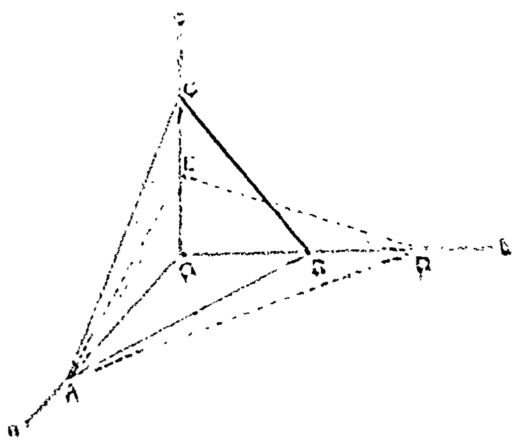


Fig. 2.8 Parameters

then the ratios of OA, OB and OC. In the parameter system of Weiss, *it is essential to chose a face whose intercepts on the crystallographic axes are taken as unit lengths for expressing the intercepts of any other face. Such a face is called a* **unit face**. The selection of unit face is arbitrary and depends upon the nature of the crystal. *The ratio of the intercepts that the unit face makes with the crystallographic axes is called* **axial ratio**. It is the convention to write the intercept on *b* axis as unity in expressing axial ratio, *e.g.*, the axial ratio for gypsum is $a:b:c = 0.6899 : 1 : 0.4124$. In obtaining the parameters of any other face on a gypsum crystal, we shall take 0.6899 as our unit of measurement along *a* axis, 1 along *b* axis, and 0.4124 along *c* axis.

For example, let us take a face *ABC* as unit face and we are to find out the Weiss parameters of the face *ADE*. From Fig. 2.8 it is seen that the face *ADE* cuts the crystallographic axis *a* at the same distance as that of unit face *ABC*, but it cuts *b* axis such that $OD = 2OB$, and cuts *c* axis such that $OE = \frac{1}{2}OC$. Thus the intercepts of the face *ADE* on the crystallographic axes *a*, *b*, and *c* are 1, 2, ½ in terms of the intercepts of unit face *ABC* on the corresponding axes. In the parameter system of Weiss, these intercepts are written before the corresponding axis. Thus, the Weiss symbol for the face [illegible] is [illegible]. If a face is parallel to a particular axis, [illegible] considered to cut the axis at infinity. Hence the sign [illegible] parameter before the corresponding axis [illegible]

face cutting b ~~the~~ and a ~~and~~ axes at 1 and 3 units respectively compared to the unit face and is parallel to c axis has the Weiss symbol as

$$(a : 3b : \infty\, c)$$

2. **Index System of Miller** *The reciprocals of parameters are called the indices* (plural of index). In the index system of Miller, these indices are witten in the order of axes a, b, c, and are given in the simplied form by clearing of fractions, if any. As for example, consider the crystal face ADE which has the Weiss symbol

$$(a : 2b : \tfrac{1}{2}c)$$

The reciprocal of the parameters, i.e, indices are

$$1, \tfrac{1}{2}, 2$$

in the axial order a, b, c. Now the indices are multiplied by 2 to *clear of the fraction. Thus, we get*

$$2, 1, 4$$

The Miller symbol for the face ADE is therefore

$$(214)$$

which is read as *two one four*. In the same way, if the Weiss symbol for a face is $(a : 3b : \infty\, c)$, then its Miller symbol is (310) which is read as *three one nought.*

As considered earlier, the unit face of gypsum crystal cuts the three axes at unequal distances, even then its Miller symbol is (111). It is due to the fact that the unit face has been defined as cutting each axis at unit length for the purpose of measuring the intercepts of other faces. Thus, the Miller symbol for the unit face ABC (Fig. 2·8) is also (111).

It may be noted that a face parallel to an axis will contain 0 (nought), the reciprocal of infinity, at the appropriate position in the Miller symbol. Again, as the Miller symbols are based on reciprocals of parameter, the larger is the figure in the Miller symbol, the nearer to the origin will face intersect the corresponding axis. In the same way, the smaller is the figure in the Miller symbol, greater will be the distance from the origin at which the face will cut the axis. The general Miller symbol is (hkl).

The Law of Rational Indices. Examination of a number of crystals led Hauy (1784) to establish a law known as the **law of rational indices.** According to this law, *the intercepts that any face of the crystal makes with the crystallographic ax are either infinite, or small rational multiples of the intercepts ma by unit face.* Thus, the Weiss symbols like $(1{\cdot}273\, a, b, 4{\cdot}52\, c)$ f any face are impossible. This law is a result of the ordered arrang ment of the constituent particles in crystals.

CLASSIFICATION OF CRYSTALS

There are three criteria on the basis of which the classifications of crystals have been done. They are as given below :

(*i*) *Classification based on the combination of elements of symmetry.*

(*ii*) *Classification based on the crystallographic axes and the angles between them.*

(*iii*) *Classification based on the nature of bonds between constituent particles.*

Let us take each type of the classification and discuss it.

(*i*) **Classification Based on the Combinations of Elements of Symmetry : Symmetry Classes or Point Groups.** As we have seen that a crystal has certain elements of symmetry like planes, axes, and centre of symmetry. These *symmetry elements form an associated group which describes the nature of symmetry in the crystal. This combination of symmetry elements is termed as* a **symmtery class or point group.** The word 'point' implies that one point, perhaps the centre of gravity remains in position during symmetry operations and the rest of crystal moves about this fixed point. All crystals having the same combination of symmetry elements belong to the same symmetry class or point group. For example, we know that the elements of symmetry for a cubic crystal are :

$$\left\{ \begin{array}{l} \text{9 Planes of symmetry,} \\ \text{13 Axes of symmetry, and} \\ \text{A centre of symmetry} \end{array} \right\}$$

If we examine the elements of symmetry of a regular octahedral crystal which contains eight equilateral triangular faces as shown in Fig. 2·9, then we shall see that the elements of symmetry possessed by it are the same as that of a cubic crystal, *i.e.*, it will also contain 9 planes, 13 axes, and a centre of symmetry. Thus, we shall say that a cubic and a regular octahedral crystal belong to the same symmetry class or point group.

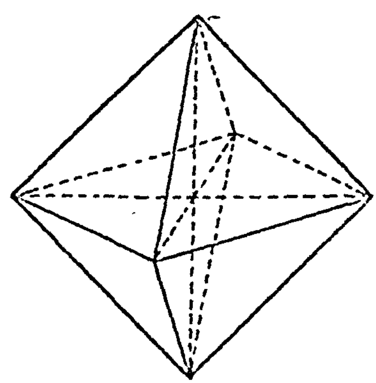


Fig. 2·9 An Octahedral Crystal

Taking in view the different elements of symmetry and the law of rational indices it was shown by Hessel (1830) that there are 32 types of symmetry classes or point groups in all. These thirty two point groups define all the ways in which the elements of symmetry about a single point may be distributed in space. The first cl

cation of crystals is therefore into thirty-two point groups. It is beyond the scope of this book to describe each type of point group.

(*ii*) **Classification Based on the Crystallographic axes and Angles between them. The Crystal Systems.** In the study of crystals it is essential to refer them to the crystallographic axes. It has been found that there are various types of these axes and the angles between them. Moreover, it is also seen that the crystals belonging to different point groups can be studied with reference to the same set of crystallographic axes. *All the crystals which can*

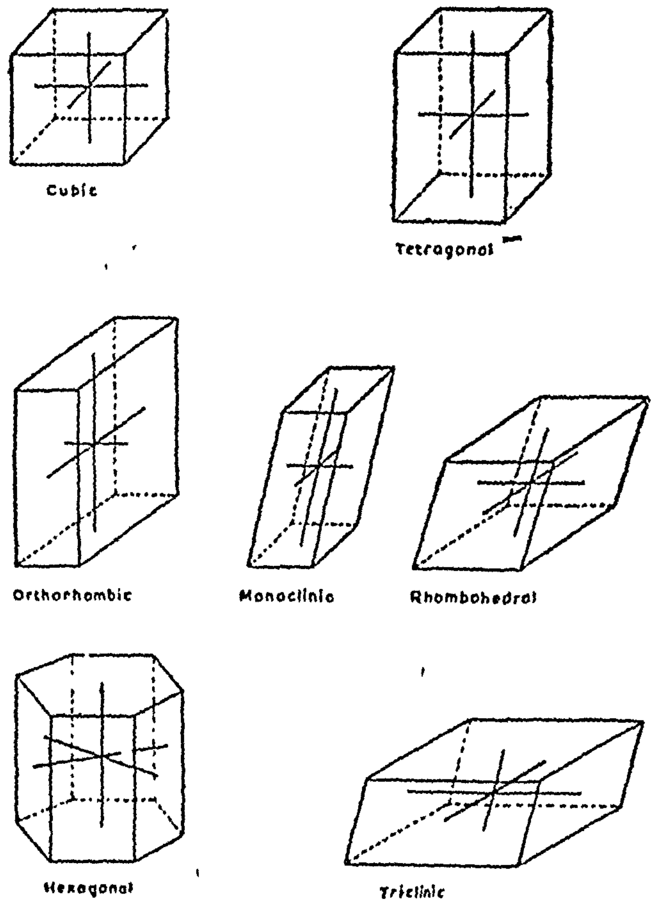


Fig. 2·10. Crystal System

be referred to the same set of crystallographic axes belong to one group known as a **crystal system.** Therefore, the second classification of crystals is, into crystal systems as shown in Fig. 2·10.

All the thirty-two classes of point groups fall into seven crystal systems. Each crystal system has a characteristic set of axes and the angles between them as shown in Table 2·2.

Table 2·2

Crystal Systems

S. No.	*Crystal System*	*Axes*	*Interaxial Angles*	*Number of point Groups*	*Examples*
1	Cubic or Regular	$a = b = c$	$\alpha = \beta = \gamma = 90°$	5	NaCl, KCl, CaF_2, Diamond
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	7	White Tin, TiO_2, $PbWO_4$
3	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	3	KNO_3, K_2SO_4, $BaSO_4$, Rhombic sulphur
4	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	3	Monoclinic Sulphur, $CaSO_4$-$2H_2O$, β-Sulphur
5	Rhombohedral Or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	5	Calcite, Quartz, $NaNO_3$
6	Hexagonal	Three equal horizontal axes. Fourth axis vertical unequal $a_1 = a_2 = a_3 \neq c$	Horizontal axes at 60° to each other, vertical axis at right angle to other three	7	Ice, Graphite. Zn, Cd
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	2	$K_2Cr_2O_7$.$CuSO_4$-$5H_2O$, H_3BO_3

It is seen from the Table 2·2 that the crystal systems range from a highly symmetrical set of three axes at right angles of the cubic system to a completely general set of three uhequal axes at three unequal angles of triclinic system.

(*iii*) **Classification Based on the Nature of Bonds between Constiuent Particles.** The consitituent particles in crystals are atoms, molecules or ions. There are following three types of crystals based on the nature of bonds between these structural units :

(*a*) **Ionic Crystals.** In these crystals the structural unit is ion and there exists electrostatic attractions between ions. Crystals of NaCl, $CuSO_4 \cdot 5H_2O$, etc., belong to this class.

(*b*) **Covalent Crystals.** These crystals are formed by molecules having covalent bonds, *e.g.*, iodine, and ice. Molecular forces of attraction are comparatively weaker in these crystats. Organic compounds also form such crystals. Sometimes giant molecules are also formed by the network of covalent bonds between atoms *e.g.*, diamond, and graphite.

(*c*) **Metallic Crystals.** These crystals are formed by atoms of metallic elements and have metallic bonds between them.

THE INTERNAL STRUCTURE OF CRYSTALS

Space Lattice and Unit Cell.

A geometrical concept, known as **lattice** has proved much useful in the study of internal structure of crystals. Space lattice constitutes the pattern upon which the internal structure of crystals is based. It was shown by Hauy (1784) that the outer shapes of the crystals is a result of an ordered array of structural units in three dimensions. Before understanding the concept of space lattice, let us understand lattice. For this, consider a simple two-dimensional design of a wall paper as shown in Fig. 2.11. It can be seen that the whole pattern consists of repetition of smaller units.

Let us choose a representative point X in the given pattern and mark the positions of similar points in whole of the design. Now if we disregard the design for the moment and consider only these points, then we shall see that they form a regular network. If we join

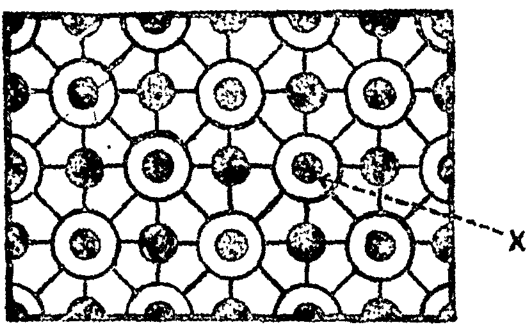


Fig. 2·11. A Two-dimensional Design on Wall paper.

these points by lines, then the whole design will be divided into small cells. Each cell will contain the same unit of pattern. The repetition of these small units forms the whole design of wall paper. It will not matter that which point is chosen as a representative point, because similar network of points will be obtained whichever point in design is chosen as a representative point. This is the fundamental property of any pattern. The choice of representative point is quite arbitrary. The network of points obtained only shows the intervals

at which the unit of pattern is repeated in the two dimensional plane. This network of points is known as **lattice.**

Similarly a crystal is a regular three-dimensional design. In a crystal also the positions of identical points can be marked and a three dimensional net work is obtained as shown in Fig. 2·12. Each point in this network has the same environment as that of any other identical point. The network of points shows the interval at which the unit of pattern is repeated in three-dimensional space. A **space lattice** *is an infinitely extended regular arrangement of points.* Each point in the space lattice has the same environment as any other similar point.

As we have seen that the straight lines joining identical point in a wall paper divide it into smaller cells Each such cell represents the unit of pattern. In the same way, straight lines joining the point in

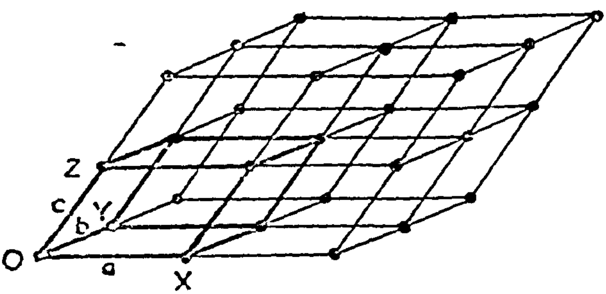


Fig. 2·12. Space Lattice and a Unit Cell

a three dimensional arrangement may be drawn as shown in Fig. 2·12. These lines divide the whole lattice into smaller three–dimensional units of pattern. Such a unit of lattice is known as **unit cell** which may be defined as *a smallest repeating unit in space lattice which results in a crystal when repeated again and again in three dimensions.* A unit cell with edges OX, OY and OZ is shown in Fig. 2.12 with thick lines. There are other ways also in which the points in in Fig. 2.12 can be joined and unit cells of different shapes may be obtained, but all these different unit cells will have the same volume. *the lengths a, b, and c of the three edges* (Fig. 2·12) *of the ch[illegible] unit cell are called its* **primitive translations.**

Types of Lattices.

It was shown by Bravais (1848) that only 14 different [illegible] lattices can be drawn in three dimensions. It means that there [illegible] only 14 ways in which similar points can be arranged in [illegible] three-dimensional order. Bravais further classified these [illegible] space lattices into *four* different types as follows :

(*i*) **Simple or Primitive lattices** are those [illegible] constituent particles are situated only at the corners [illegible]

(*ii*) **Base-centred Lattices** are those in which [illegible] located at the centres of any two parallel faces [illegible] particles at the corners of unit cell.

(*iii*) **Body-centred Lattices** are those in which a particle is located at the centre of the cell in addition to those at the corners of the cell.

(*iv*) **Face-centred Lattices** are those in which particles are located at the centre of each face besides those at the corners of the cell.

All these types of space lattices fall into seven crystal systems as shown in Table 2·2.

Table 2·2
Distribution of Lattice Types in Crystal Systems

System	*Distribution of Lattice Types*	*Total number of Lattice Types*
1. Cubic	Simple, Body-centred, and Face-centred	3
2. Tetragonal	Simple and Body-centred	2
3. Orthorhombic	Simple, Base-centred, Body-centred, and Face-centred	4
4. Monoclinic	Simple and base-centred	2
5. Rhombohedral	Simple only	1
6. Hexagonal	Base centred only	1
7 Triclinic	Simple only	1

The simple, Face-centred and Body-centred, lattices of cubic system are shown in Fig. 2·13 as an illustration.

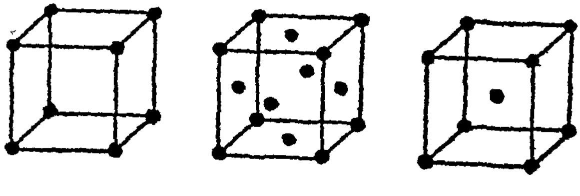


Fig. 2·13. Simple, Face-centred and Body-centred, cubic Lattices.

It can be noted from Fig. 2·12 that one point belongs to each simple unit cell. Although there are eight points at the corners of a unit cell, but it should be remembered that 8 unit cells meet at a corner and the point is shared equally by each cell. Thus on an average a simple unit cell contains only *one* point. In a body centred lattice, there is an extra point in the centre of each cell apart from those at the corners. Thus, each body-centred unit cell contains *two* points. In the same way it can be calculated that a face centred lattice contains *four* points. In crystals these points represent the structural units like atoms, molecules or ion pairs. With the concept of space lattice and unit cell it has been possible to calculate the interatomicdistance in many crystals. The following example will make it clear.

Example 2 1. *Aluminium crystallises with face centred cubic lattice. If the density of Aluminium is 2·69, calculate the distance of closest approach of Al atoms in the crystal. Atomic weight of Al=26·98).*

Solution. Since the crystal is a face-centred one, a unit cell contain 4 atoms.

We know that

$$\text{Mass of 4 atoms of Al} = \frac{4 \times \text{gm atomic weight}}{\text{Avagadro Number}}$$

Here

gm atomic weight = 26·98 gm

$$\therefore \quad \text{Mass of 4 Al-atoms} = \frac{4 \times 26{\cdot}98}{6{\cdot}023 \times 10^{23}}$$

$$\text{Volume occupied by 4 atoms of Al} = \frac{\text{Mass of 4 Al atoms}}{\text{Density of Al}}$$

Here Density of Al = 2·69

$$\therefore \quad \text{Volume occupied by 4 Al atoms} = \frac{4 \times 26{\cdot}98}{6{\cdot}023 \times 10^{23} \times 2{\cdot}69}$$

$$= 64 \times 10^{-24} \text{cc}$$

Hence, the volume of cubic unit cell $= 64 \times 10^{-24}$ cc

$$\text{The edge of cubic unit cell} = \sqrt[3]{\text{volume of unit cell}}$$

$$= \sqrt[3]{64 \times 10^{-24}}$$

$$= 4 \times 10^{-8} \text{ cm} = 4 \text{ Å}$$

$$\text{The length of face-diagonal} = \sqrt{2(\text{Edge})^2}$$

$$= \sqrt{2 (4)^2} \text{ Å}$$

$$= 4\sqrt{2} \text{ Å}$$

$\therefore$ The distance between closest atoms

$$= \tfrac{1}{2} \text{ (length of face diagonal)}$$

$$= \tfrac{1}{2} \times 4\sqrt{2} = 2{\cdot}83 \text{ Å}$$

Lattice Places. It can be seen from Fig. 2·12 that *the points in a space lattice can be arranged in a series of parallel and equidistant planes called* **lattice planes** or **net planes.** A set of such planes is shown by dotted area in Fig. 2·14. It is not the only way in which the points in the space lattice (Fig. 2·14) can be arranged in parallel and equidistant planes. In fact, there are a number of ways and there may be other lattice planes also with different spacings, but they will be parallel. Another set of lattice planes is shown by horizontal lines. The faces of crystals are found to be parallel to lattice planes. The most common faces correspond to those planes which contain the largest number of points representing the structural units.

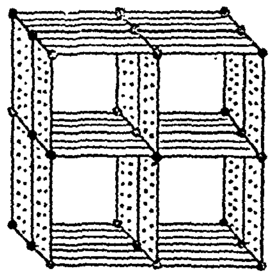


Fig. 2·14. Lattice planes

CRYSTAL STRUCTURE BY X-RAY DIFFRACTION

Basic Principle of Diffraction Methods.

The basic principle of diffraction methods depends upon interference. The phenomenon of interference occurs when a wave motion is scattered from various centres simultaneously. We can take the example of the interference of monochromatic visible light, when it passes through a number of closely spaced slits as shown in Fig. 2·15. Slits S_1 and S_2 act as point sources and the light is scattered from them in all directions. It can be seen from Fig. 2·15 (*a*) that the waves will be in phase if they move in such a direction that their path difference after emerging from the slits is $n\lambda$. The two waves will reinforce each other in such directions resulting in **constructive interference** and more light will be seen. Thus, the essential condition for constructive interference is that the diffracted ray must be in the direction θ [Fig. 2·15 (*a*)] such that

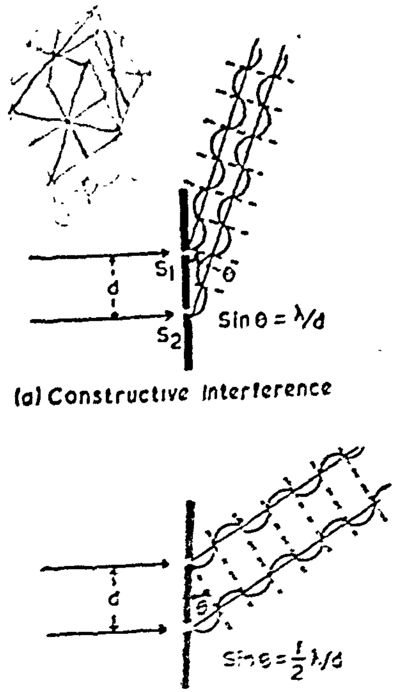
$$\sin\theta = \frac{n\lambda}{d} \qquad \ldots(2\cdot1)$$

where λ is the wave length of light, d is the distance between slits S_1 and S_2, and $n = 1,2,\ldots$ In Fig. 2·15 (*a*), n is seen to be equal to 1. Eq. (2·1) shows that there are various values of θ at which constructive interference can occur according as $n = 1,2,3,\ldots$

In other directions the diffracted ray will be out of phase to different extents and destructive interference will result. The waves will cancel each other in these directions and less light will be seen.

The two waves will be completely out of phase, if they move in such direction that their path difference is $\lambda/2$ as shown in Fig. 2·15 (*b*).

As the value of $\sin \theta$ ranges from 0 to 1, it is clear from Eq. (2·1) that the value of $n\lambda/d$ must also range from 0 to 1. It is concluded, therefore, that *d and λ must be of the same order*, because n is a small integer. Thus, *diffraction of light will occur only if the spacing of the scattering centres is of the same order as the wave lengths of light used*. On this basis, Laue (1912) gave a brilliant suggestion that a crystal may act as a three-dimensional grating for the diffraction of X-rays, because the spacing d of the scattering units (atoms, molecules, or ions) in a crystal may be of the same order (10^{-8}cm) as the wave length λ of X-rays. Knowing the wave length λ of X-rays the spacing d between the structural units of crystals can be found by measuring the direction θ of the diffracted beam.



(a) Constructive Interference

(b) Destructive Interference

Fig. 2·15.

Diffraction of X-rays by Crystals.

Friedrich and Knipping started the experimental test, on the suggestion of Max von Laue, at the university of Munich for the diffraction of X-rays by crystals. A narrow beam of X-ray was passed through a crystal of zinc blende, ZnS and allowed to fall on a photographic plate. They obtained a pattern of spots around the central intense spot. Laue showed that the positions of these spots were in consistence with the diffraction of X-rays by cubic arrangement of scattering units in the zinc blende crystal. This discovery simultaneously established the following two facts :

(*i*) the X-rays could be diffracted like light possess wave nature, and

(*ii*) the crystals consist of an ord tural units with equal spacing.

When the news of Friedrich's work reached England, it was immediately taken up by W. L. Bragg and his father W. H. Bragg. These workers applied extensively the X-ray diffraction to study the *internal structure of many crystals*. We owe greatly to them for the early development of the subject. Their treatment will now be considered in detail.

The Bragg Equation. Braggs gave a treatment of X-ray diffraction by a crystal which is simpler than the Laue theory. They suggested that the crystal should be used as a reflection grating rather than a transmission grating. Every structural unit (atom, molecule or ion) will scatter X-rays depending upon the number of extranuclear electrons. Thus, every lattice plane containing these structural units behaves to the X-rays just as does a line in a diffraction grating to visible rays. The nature of the spectra produced by a line grating depends upon the distance between successive lines. In the same way, the nature of X-ray diffraction depends upon the spacing between the successive lattice planes.

When the rays from an X-ray tube, or **primary rays,** impinge on a crystal, the electrons of material particles in the crystal are excited. Thus, these material particles become a secondary source of X-rays. They emit X-rays of the same wave length but of weaker intensity. These rays are called **secondary rays.** As these rays have a very weak intensity, their presence can only be detected if they combine by constructive interference and thus increase their intensity. The condition for this constructive interference may be worked out in the following manner.

Consider a section through a crystal lattice as shown in Fig. 2·16. Lattice planes a_1, a_2, a_3, etc., are perpendicular to the plane of this page. Material particles are represented as points in these planes. Let a parallel beam of X-rays (Primary rays) strikes these planes at an angle θ. This angle is between the direction of rays and the plane of incidence, hence θ is called the **glancing angle.** The part of the beam, *e.g.*, ray AB, will be reflected by the plane a_1 at B in the direction BC. Another ray DE will penetrate the crystal and be

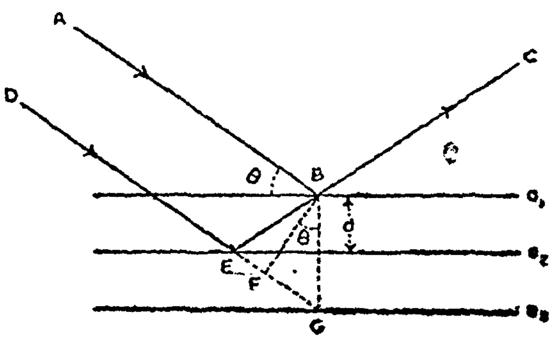


Fig. 2·16. X-Ray Reflection by Lattice planes.

reflected by the plane a_2 at E in the direction EC. Similar reflections will occur at other planes. Thus, it is clear that the beam which emerges from the crystal in the direction BC is made up of a number of rays which have travelled various distances through the crystal. These emerging rays will reinforce one another only if the path difference is equal to an integral multiple of the wave length λ of X-rays, *i.e.*, $n\lambda$, where n is a whole number. To calculate the path difference between the rays ABC and DEC, from B draw perpendicular BG on the plane a_3, and BF on EG. The path difference $\triangle$ between ABC and DEC is obviously,

$$\triangle = (DE+EB)-AB \qquad ...(2\cdot2)$$

But $\quad AB = DF = DE+EF$

Putting the value of AB in Eq. (2·2), we get

$$\triangle = (DE+EB)-(DE+EF)$$

or $$\triangle = EB-EF \qquad ...(2\cdot3)$$

From the geometry of the triangle BEG,

$$EB = EG$$

Hence, putting EG instead of EB in Eq. (2·3) we get

$$\triangle = EG-EF$$

$$\triangle = FG \qquad ...(2\cdot4)$$

From the geometry of the Fig. 2·16, it can be clearly seen that $\angle$FBG is the same as glancing angle θ. From the triangle BFG,

$$\sin\theta = \frac{FG}{BG}$$

or $$FG = BG \sin\theta$$

or $$FG = 2d \sin\theta \qquad ...(2\cdot5)$$

where d is perpendicular distance between successive lattice planes. From Eqs. (2·4) and (2·5)

$$\triangle = 2d \sin\theta$$

For a maximum reflection, the path difference $\triangle$ must be equal to $n\lambda$. Therefore, the condition for maximum reflection is given by

$$2d \sin\theta = n\lambda \qquad ...(2\cdot6)$$

This is the **Bragg Equation.** It applies to rays reflected from other planes also. If θ, n and λ are known, then d can be calculated. For homogeneous X-rays and a definite set of lattice planes, λ and d are fixed. Hence, the extent of diffraction depends upon θ, the glancing angle. As θ is gradually increased, a series of maximum reflections occur corresponding to $n=1, 2, 3,...$ These diffraction maxima are called *first, second, third*, etc., *order* according as $n=1, 2, 3$, etc. The glancing angle θ can be measured corresponding to various order and d, the spacing between the lattice planes can be determined using the Bragg Equation. The following example will make it clear.

Example 2·2. *The first order diffraction maximum of the Ka rays of palladium, reflected from (200) planes of NaCl crystal occurs at the glancing angle of 5·9°. If the wave length of the Ka rays of palladium is 0·581 Å, calculate the spacing between (200) planes of NaCl crystal.*

Solution. We know that

$$2d \sin \theta = n\lambda$$

Here $\theta = 5{\cdot}9°$, therefore $\sin \theta = 0{\cdot}103$

$n = 1$, and $\lambda = 0{\cdot}851\text{Å}$

$\therefore$ $2 \times d \times 0{\cdot}103 = 1 \times 0{\cdot}581$

or $$d = \frac{0{\cdot}581}{2 \times 0{\cdot}103} = 2{\cdot}82\ \text{Å}$$

EXPERIMENTAL METHODS OF CRYSTAL ANALYSIS

There are various methods for the analysis of crystal structure. The three principal methods are :

1. Bragg's method
2. Rotating crystal method, and
3. Powder method.

Now we shall describe each of the above methods.

1. The Bragg Method. The Bragg's X-ray spectrometer is outlined according to the following scheme. Primary X-rays obtained from a molybdenum anticathode X of an X-ray tube are passed through slit S_1 and allowed to fall on a known face of crystal C. The crystal is mounted on a rotating table and its position can be read on the vernier scale V. The secondary rays from the crystal are allowed to enter the ionisation chamber I after passing through another slit S_2. The ionization chamber is filled with a gas, e.g., SO_2. Two electrodes A_1 and A_2 of the ionization chamber are connected to a battery B through an electrometer E. When ionization of the gas takes place due to the entry of X-rays, there is a flow of current in the circuit measured by electrometer. The reflected rays enter the

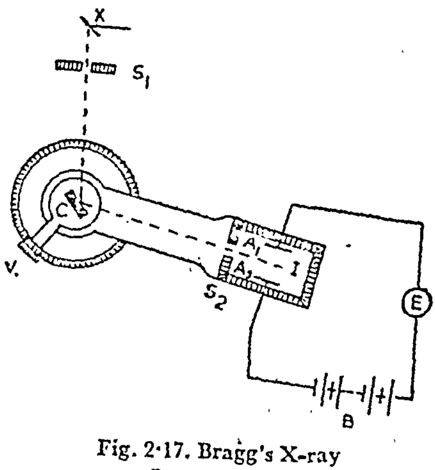


Fig. 2·17. Bragg's X-ray Spectrometer.

ionisation chamber for all positions of the crystal because the arm carrying the chamber rotates about the axis of instrument at double the rate of rotation of the crystal.

Starting with small glancing angle θ and gradually increasing it, the readings in the electrometer are taken for various values of θ. The readings of the electrometer give a measure of the intensity of X-rays entering the ionisation chamber. Sharp reflection maxima are obtained for those values of θ which satisfy the Bragg equation, $2d \sin\theta = n\lambda$, where d is the spacing of lattice planes parallel to crystal face exposed to primary X-rays. Knowing the value of λ, d can be calculated for these lattice planes. This procedure is repeated for all important lattice planes of the crystal for the analysis of crystal structure.

This method is tedious and requires crystals with well developed faces, but the interpretation of the results is quite easy. This method is used when all other methods fail.

2. The Rotating Crystal Method. This method was developed by Polanyi (1921). In this method a small crystal is exposed to monochromatic X-rays and is rotated at the speed of 10—15 rotations per hour round an axis parallel to one of the crystallographic axes. As the crystal is rotated, various planes come one after another into suitable positions for diffraction to occur. Corresponding spots are produced on cylindrical photographic film placed around the crystal C as shown in Fig. 2.19.

The geometrical interpretation of rotation photographs is more complex. However, there is a very striking feature of the photographs. This is the arrangement of spots in horizontal lines, when a zone axis of crystal is parallel to the axis of rotation. These horizontal lines containing bright spots are called **layer lines** and have a simple explanation. Let c be the axis around which the crystal is rotated as shown in Fig. 2·18. PQ represents the spacing d between successive lattice planes. The incident rays AP and BQ are perpendicular to the axis of rotation. In order that

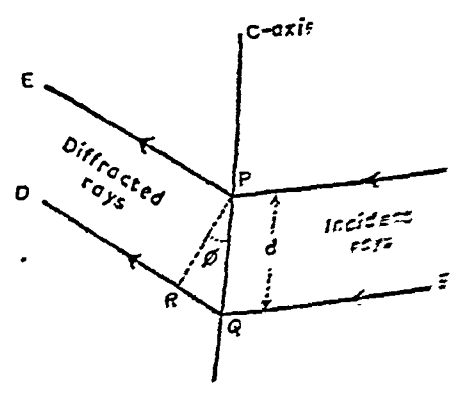


Fig. 2·18. The Principle of Rotating Crystal Method.

structive interference takes places, the path difference between the rays scattered from P and Q in the direction PC and QD respectively should be an integral multiple of wave-lentgh λ of X-rays. This path difference, QR $= d \sin \phi = n\lambda$, where ϕ is $\angle$RPQ as shown in Fig. (2·18). This condition determines the angle which the diffracted rays PC and QD make with the axis of rotation. On rotating the crystal, it will pass through various positions suitable for diffraction. All lattice planes with the same spacing PQ in the direction parallel to the axis of rotation will produce spots lying on a horizontal line on the photographic film.

Now consider the Fig. 2·19 in which crystal c is rotated around the crystallographic axis C. Lattice planes which are parallel to this axis may be represented by the general Mirlle indices ($hk0$). These planes will reflect the rays horizontally and give spot on the so called **zero,layer line** passing through the central spot in the photograph. Lattice planes inclined to the C axis will have the Miller indices like ($hk1$), ($hk2$), etc., and will produce first, second, etc., layer lines symmetrically above and below the zero layer line. Lattice planes perpendicular t o the C-axis will give no spots. The beams producing the spots of a 'given layer line lie on a cone which cuts the cylindrical film giving rise to horizontal lines. The spacing d of the lattice planes is given by

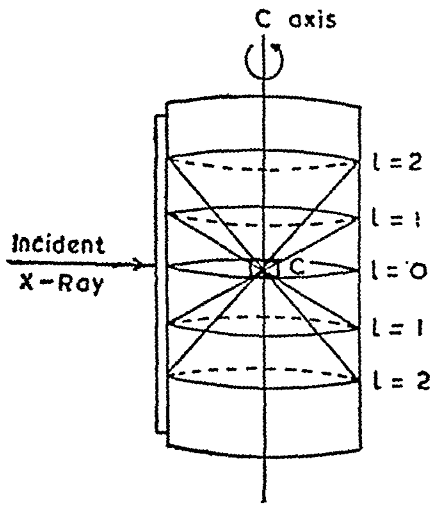


Fig. 2·19. Layer Lines of a Rotation Photograph on Cylindrical Film

$$d = \frac{n\lambda}{\sin \phi}$$

where n is the number of layer line (1,2,3,......etc). The angle ϕ is found by the relation

$$\tan \phi = \frac{e_n}{R}$$

where e_n is the vertical distance of nth layer line from zero line and R is the radius of cylindrical film.

The Powder Method. This method was developed by Debye and Scherrer. The sample in this method is in the powdered form so that the individual crystals are very small and oriented at random. The experimental arrangement is shown in Fig. 2·20 (*a*). The powdered sample is filled in a thin-walled glass capillary C. A narrow beam of monochromatic X-rays defined by slit S is allowed to fall upon the specimen in C. The crystals in the sample will be present in all possible orientations. For each set of lattice planes of the crystal, there will be some angle θ which satisfies the Bragg equation, hence some of the crystals will always have this orientation. Therefore, a diffracted beam will come out at appropriate angle as shown in Fig. 2·20 (*a*). The crystalline particles which produce the diffracted beam must be so set that the glancing angle θ is correct, but they may have any orientation around the direction of incident beam as axis. Hence the diffracted rays lie on a circular cone as shown in Fig. 2·20 (*b*). This cone intersects the cylindrical film surrounding the specimen in the form of arcs or lines. When the film is unrolled, it gives the appearance as shown in Fig. 2·20 (*c*).

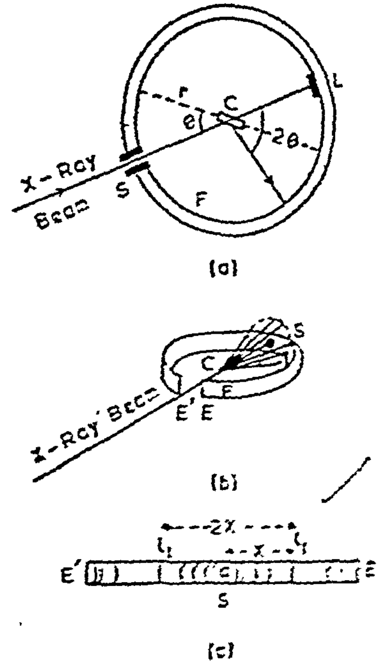


Fig. 2·20 X-ray Powder Method.

When the powder photograph is obtained, then the next step is to index the lines on it, *i.e.*, assigning each the set of lattice planes responsible for its origin. For this purpose, the distance, say of the line l_1 as shown in Fig. 2·20 (*c*) is measured accurately. This is usually done by halving the distance $2x$ between two reflections on both sides of the central spot. If the radius of the film is r (Fig. 2·20 (*a*)), then the circumference $2\pi r$ corresponds to scattering angle of 360°. Hence,

$$\frac{x}{2\pi r} = \frac{\theta}{360} \qquad ...(2·7)$$

Thus, θ can be calculated from Eq. (2·7) and ... spacing d between the lattice planes can be obtained from ... (2·6).

This method has a great advantage that ...

2·22 (*a*) is cut by three mutually perpendicular planes into eight tiny cubes and additional single carbon atoms shown as black circles in figure, are put in the centres of two upper cubes (front side right-handed and back side left-handed) and two lower cubes (front side left-handed and back side right-handed), then the structure of diamond is produced as shown in Fig. 2·22 (*a*). The additional black circled atom in a small cube is in such a position that the four white circled carbon atoms at the corners of this small cube may be visualized to be located at equidistant corners of a regular tetrahedron as shown in Fig. 2·22 (*b*). If the lattice shown in Fig. 2·22 (*a*) is extened in all directions, it is seen that black circled atoms also lie in a face-centred cubic lattice. Thus the space lattice of diamond may be visualized as two interpenetrating face centered cubic lattices. Each carbon atom is surrounded tetrahedrally by four carbon atoms at equal distances. The distance between two closest carbon atoms has been found to be 1·54 Å, which is identical with C—C bond in ethane. Thus, all the carbon atoms in diamond are joined to each other by strong covalent single bonds. Hence a diamond crystal may be regarded as a single carbon molecule for which the term **macromolecule** is used. This accounts for the extremely high hardness of diamond.

Graphite. It crystallises in hexagonal system. A unit cell of graphite is shown in Fig. 2·23. The height of unit cell is 6·82 Å. The space lattice of graphite consists of parallel layers of carbon atoms. The spacing between the layers is 3·41 Å which does not correspond to chemical bond. Within each layer the carbon atoms are arranged in flat hexagons. The C—C distance within each sheet

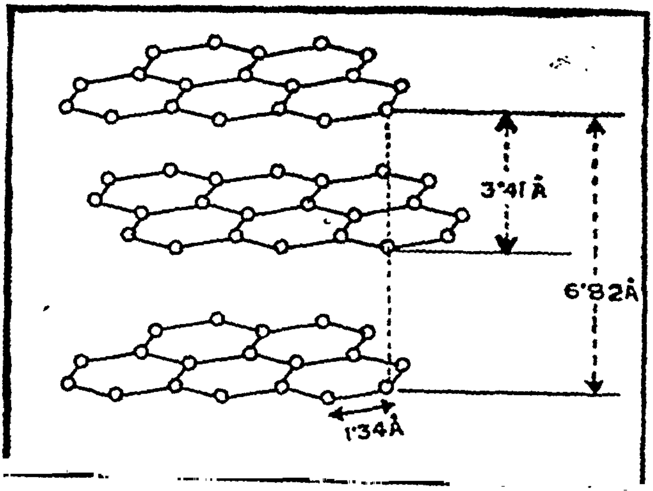


Fig. 2·23. Crystal Lattice of Graphite.

is 1·34 Å which is identical with that in anthrane. We can distinguish two kinds of electrons in graphite. The σ electrons form strong covalent bonds by sp^2 hybridization in the sheet. The π electrons between the sheets are delocalized and are free to move over all the atoms imparting a high conductivity to graphite. The binding between the layers is much weaker giving a slippery and flaky nature to graphite.

TEST YOUR KNOWLEDGE

1. **Give a term for each of the following :**

   (*i*) Substancects giving the same value of physical property in all directions.

   (ii) Surfaces by which a crystal is bounded.

   (*iii*) Geometrical expressions of symmetry operations.

   (*iv*) The ratio of the intercepts that the unit face makes with crystallographic axes.

   (*v*) An infinitely extended regular arrangement of constituent particles.

   (*vi*) Horizontal lines containing bright spots on a rotating crystal photograph.

   (*viii*) Lattices in which the particles are located at the centre of each face besides those at the corners of the cell.

2. **Fill in the blanks :**

   (*a*) The crystallographic axes intersect at the......

   (*b*) The.........of parameters are called the indices.

   (*c*) Two waves will be completely out of phase if their path difference is.........

   (*d*) A unit cell of sodium chloride consists of ......cubic lattice.

   (*e*) The diffraction of light will occur only if the spacing of the scattering centres is of the same order as the.........of light used.

   (*f*) There are, in all,.........lattices that can be drawn in three dimensions.

   (*g*) A face parallel to any axis will contain.........at the appropriate position in its Miller symbol.

   (*h*) A crystal may have either.........or no centre of symmetry.

   (*i*) On an average a simple unit cell contains.......,..structural unit.

KEY

1. (*i*) Isotropic substances (*ii*) Faces (*iii*) Elements of symmetry (*iv*) Axial ratio (*v*) Space lattice (*vi*) Layer lines (*vii*) Face centred lattices.

2. (*a*) origin (*b*) reciprocals (*c*) $\lambda/2$ (*d*) face-centred (*e*) wavelength (*f*) fourteen (*g*) 0 (*h*) one (*i*) one.

QUESTIONS

1. Distinguish between—

   (*i*) Crystalline and amorphous substances.

   (*ii*) Isotropic and anisotropic substances.

. Define the terms :

Faces, Edge, Interfacial angle, Solid angle, Form, Zone, Crystallographic axes, Parameters, Point group, Body centred lattice, Lattice plane, Glancing angle, Macromolecule.

. What do you understand by 'symmetry' and 'elements of symmetry'? Explain

(*i*) Plane, (*ii*) Axis, and (*iii*) Centre, of symmetry. Show the various elements of symmetry in a cube with diagrams.

. What is a 'Crystallographic designation'? Explain the following systems of crystallographic designation :

(*a*) Parameters system of Weiss.
(*b*) Index system of Miller.

. Convert the following Weiss symbols of faces into Miller symbols :

(*i*) $a : 3b : c$, (*ii*) $2a : b : \infty c$, (*iii*) $3a : \infty b : c$

[Ans. (*i*) (313), (*ii*) (120), (*iii*) (103)]

. What are the various criteria on the basis of which the classification of crystals has been done? Describe fully the classification of crystals into crystal systems.

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. Explain with suitable examples the 'space lattice' and 'unit cell' What are simple, face-centred and body-centred cubic lattices? Give diagrams.

3. Give the underlying principle of diffraction methods for crystal structure determination. Describe (*i*) Rotating crystal, and (*ii*) Powder methods.

) Derive the Bragg equation and give the Bragg method for crystal structure-determination describing X-ray spectrometer.

1. Describe the crystal structures of NaCl and KCl. How does the X-ray spectrum of KCl correspond to simple cubic lattice, whereas it actually consists of face-centred cubic lattice.

1. What are 'ionic crystals'? What is the evidence that the structural units in NaCl crystal are Na^+ and Cl^- ions, and not NaCl molecule?

2. What do you mean by 'covalent crystals'? Explain the space lattices in the crystals of diamond and graphite.

3. Give reasons for the following :

(*i*) A glass prism, though possessing elements of symmetry, is not a crystal.
(*ii*) All crystals aro anisotropic, but those of cubic system are isotropic.
(*iii*) There are eight structural units at the corners of a simple unit cell, yet a unit cell is said to possess only one structural unit.
(*iv*) Diffraction will occur only if the spacing of the scattering centres is of the same order as the wave length of light used.
(*v*) The diffracted rays in powder method lie on a circular cone.
(*vi*) The first order reflection from (111) planes in a NaCl crystal is weak.
(*vii*) Diamond and graphite both contain carbon atoms, yet diamond is very hard and graphite is soft.
(*viii*) The unit face of gypsum crystal cuts the three crystallographic axes at unequal lengths, even then its Miller symbol is (111).

4. CsCl crystallises with body-centred cubic lattice, the unit cell of which contains one Cs^+ and one Cl^- ion. If the density of salt is 3·97 gm/cc, find the length of one edge of the unit cell. (Formula weight of CsCl = 168·4).

[Ans. 4·13 Å]

15. Calculate the longest wave-length of X-rays that can be used to determine the spacing of 1 Å between lattice planes of a crystal by Bragg method.

[Ans. 2Å]

16. The reflection maxima from a set of lattice planes of β—corundum for Kα rays of rhodium occur at the following angles for various orders :

n	2	4	6	8
θ	1·46'	3°32'	5°19'	7°6'

Show that these data satisfy the Bragg equation.

17. Cesium crystallizes with body centred cubic lattice, the unit cell of which contains one kind of ion at the centre and the other kind of ions located at the corners. What is the ratio of cesium to chloride ions in the unit cell. Explain. [Ans. 1 : 1.]

18. The spacing of (100) planes of KCl is 3·152 Å. At what angle would first order diffraction from these planes be observed if X-rays of wave length 1·537 Å are used.

[Ans. 14·7'.]

19. CsBr crystallizes with body-centred cubic lattice. Calculate the length of its unit cell edge, if its density is 4·49 gm/cc.

(Formula wt. of CsBr is 212·81) [Ans. 4·29 Å]

20. The characteristic Kα rays of Cr. Fe and Ni are of wave length 2·2909, 1·9373, and 1·6591 Å respectively. Find out (*a*) which of these rays can be used to determine a spacing of lattice planes equal to 1 Å and (*b*) what would be the largest value of θ.

3

Chemical Kinetics

Introduction.

Chemical reactions proceed with wide range of rates. Some reactions, for example, detonation of an explosive takes place almost instantaneously. Ionic reactions, involving no change in oxidation states, *e.g.*, acid-base neutralizations, precipitation of AgCl, etc., also go to completion in a fraction of second. Some reactions such as ionic oxidation—reduction reactions in which the actual transfer of electrons, atoms, or group of atoms takes place are generally slow. For example, reaction between permangnate and oxalic acid or H_2O_2, precipitation of Hg_2Cl_2 by the addition of $SnCl_2$ in $HgCl_2$ solution proceed with slow rates. There are certain reactions, such as weathering of rocks and reactions in earth's crust are very slow and continue for several years. For all practical purposes it seems that no reaction is being taking place. It has been found that not only different reactions proceed with different rates but the rate of a particular reaction can be varied by varying the conditions such as concentration and temperature. Thus, it has become essential to know how fastly a reaction proceeds and what factors influence the reaction rate so that the reaction may be made to proceed under control, *i.e.*, at any desired rate. **Chemical kinetics** embraces this problem and is defined as *that branch of chemistry which deals with the rates of chemical reactions and their mechanisms.* Now we shall discuss what are meant by the **rate of reaction** and the **reaction mechanism.**

Rate of Reaction

The **rate of a chemical reaction** may be defined as *the change in concentration of a reactant or a product per unit time.* In a

chemical reaction the concentration of a reactant decreases and that of a product increases as the reaction progresses, as shown in Fig. 3·1. Accroding to the law of mass action, the rate of a chemical reaction depends on the concentration of the reactants. Since the concentration diminishes with time, the rate of reaction also diminishes. Hence, the reaction velocity usually does not remain constant but changes with time as shown in Fig. 3·2. It is evident from the figure that in the initial stages. the reaction velocity decreases rapidly and then slowly and ultimately becomes negligibly smaller but never reaches zero because curve is asymptotic to the time axis. Theoretically this means that the reaction will take infinite time for its completion but in actual practice, the rate becomes negligibly small after some time and for all practical purposes, the reaction may be considered as complete after that time.

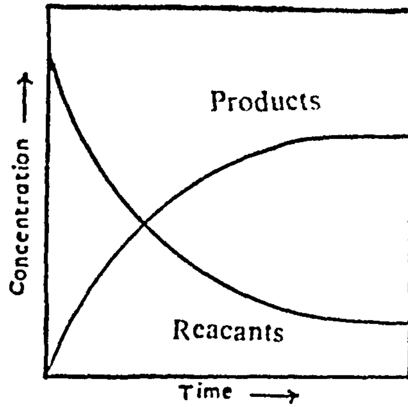

Fig 3·1. Dependence of concentrations of Reactants and Products in a Chamical Reaction on time.

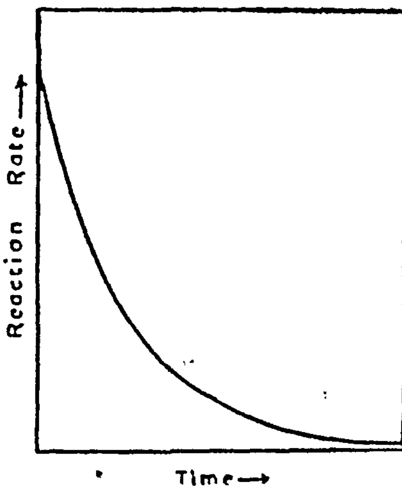

Fig. 3·2. Time Dependence of the Reaction rate.

Since the rate is constantly decreasing, it is meaningless to talk about a general rate of a reaction. If $\triangle c$ is the change in concentration of a reactant or a product in a small time interval $\triangle t$, then the average rate of reaction, $\bar{v}$ during that interval is given by

$$\bar{v} = \pm \frac{\triangle c}{\triangle t}$$

Since the concentration of reactants decrease and those of products increase, the concentration changes of reactants are taken as *negative* and those of products as *positive*. This sign convention is so chosen that the numerical value of the rate of reaction always becomes a positive quantity.

The true rate of reaction, v at a given moment can be obtained if we make $\triangle t$ infinitesimally small. In the language of cal- when $\triangle t \to 0$, the above expression converges to

$$v = \pm \frac{dc}{dt} \qquad ...(3\cdot1)$$

Here, dt represents infinitesimal time interval and dc, the corresponding infinitesimal concentration change. The quantity dc/dt is known as the **derivative of concentration with respect to time** and truly represents the instantaneous rate of change of concentration at a given moment. To express rates of reactions, such time derivatives are used.

Let us consider a simple reaction

$$A+B \rightarrow C+D \qquad ...(3\cdot2)$$

The concentration of a substance is generally expressed either by writing the formula of the substance as the subscript of c or by enclosing the formula in square bracket. For example, the concentration of A can be represented as c_A or [A]. Using Eq. (3·1), the rate of reaction may be denoted by

$$v = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \frac{dc_C}{dt} = \frac{dc_D}{dt} \qquad ...(3\cdot3)$$

or $$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} \qquad ...(3\cdot4)$$

The stoichiometry* of reaction (3·2) shows that the concentrations of A and B decrease at the same rate and is exactly equal to the rate at which the concentrations of C and D increase.

Let us consider the following reaction :

$$2A \rightarrow C+D \qquad (3\cdot5)$$

The Stoichiometry of this reaction shows that the rate of disappearance of A is twice the rate of formation of C and D. Hence, we can write

$$v = -\frac{1}{2}\frac{d[A]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} \qquad ...(3\cdot6)$$

From this example, it is evident that the concentrations of the various species in chemical reaction may change at different rates. Here, a question arises—Will the rate of reaction be equal to the rate at which the concentration of A changes or the rate at which the concentration of C changes ? The answer to the question can be given by considering the following general reaction.

$$aA+bB+... \rightarrow mM+nN+...... \qquad (3\cdot7)$$

The relation between the various derivatives can be written as

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{m}\frac{d[M]}{dt} = \frac{1}{n}\frac{d[N]}{dt} \qquad ...(3\cdot8)$$

*Stoichiometry is the quantitative weight relationships that are expressed in chemical equations.

Here all the quantities are equal and hence any one of them can represent the rate of the reaction. Thus, the **rate of reaction** may be defined as *the derivative of concentration with respect to time divided by proper stoichiometric coefficient and converted to a positive quantity.* For example, in the following reaction :

$$N_2 + 3H_2 \rightarrow 2NH_2$$

The rate of reaction $= -\dfrac{d[N_2]}{dt} = -\dfrac{1}{3}\dfrac{d[H_3]}{dt} = \dfrac{1}{2}\dfrac{d[NH_3]}{dt}$.

The rate may be determined by measuring the concentration change of either one of the reactants or one of the products at various times. The concentration is then plotted against time. The rate of reaction at a particular instant can be obtained by the slope of the tangent drawn at that point in question. This gives the instantaneous rate of reaction at that particular moment and concentration. Fig. 3·3 shows two curves : (*a*) for the reactant A and (*b*) for the product C. The slopes dc_A/dt of curve (*a*) and dc_C/dt of curve (*b*) at a particular time t give the rate of reaction at that time. The value of dc_A/dt will be negative and hence by putting a negative sign before it, the value becomes positive.

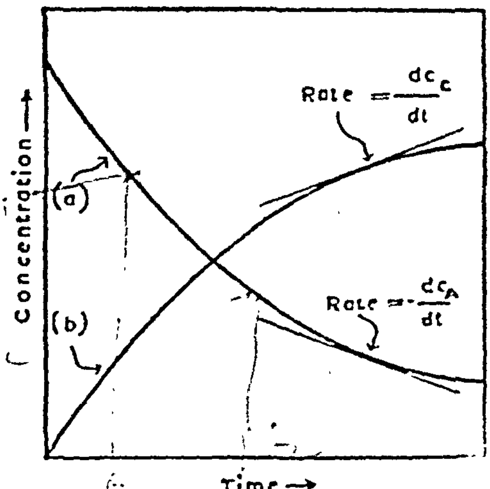

Fig. 3·3. Determination of Rate of reaction from the Concentration-Time Plots.

There is another convenient way of expressing the rate of reaction. Suppose the initial concentration of A is a. Let x be the decrease in concentration of A upto time t. Then the instantaneous concentration of A at time t, *i.e.*, c_A will be equal to $(a-x)$.

Hence, the rate of reaction at this moment will be

$$-\frac{dc_A}{dt} = -\frac{d\,(a-x)}{dt} = \frac{dx}{dt} \qquad ...(3{\cdot}9)$$

Thus, the rate of reaction may also be denoted by dx/dt, where x is the decrease in the concentration of the reactant or the increase in the concentration of the product.

The rate of reaction may also be defined by using variables in other than the concentrations. For example, in case of gaseous reactions the reaction rates may be expressed in terms of the change in partial pressure per unit time. Thus, the rate of the following reaction

$$H_2(g)+I_2(g) \rightarrow 2HI(g).$$

may be given by

$$-\frac{dp_{H_2}}{dt}, -\frac{dp_{I_2}}{dt}, \frac{dp_{HI}}{dt}$$

Similarly in case of racemization, inversion or mutarotation reactions, the rate is defined by the change in optical rotation.

Measurement of Reaction Rates

The extent of reaction is a function of time and can be determined by a number of methods. As already discussed, the reaction rate can be determined with respect to any of the reactants or products. For accurate measurements, the temperature of the reaction must be kept constant. This can be done by carrying out the reaction in a thermostat. Further, the measurement should be such that it should not disturb the course of reaction.

The course of reaction can be followed by measuring the concentration by chemical analysis methods (gravimetric or volumetric). or by noting the change in physical properties, such as refractive index, optical density, specific volume, specific rotation, viscosity, pressure in case of gases. pH, electrical conductance, etc.

For example, in case of the decomposition of N_2O_5 in solution

$$2N_2O_5 \rightarrow 2NO_2+O_2(g)$$

the course of reaction can be followed by measuring the volume of O_2 evolved from time to time. In the reactions involving the change in ionic species with time, the course can be followed by measuring the conductance at different times. Reactions in which coloured species are involved can be studied by measuring absorption of light from time to time. For some reactions such as hydrolysis of an ester, direct chemical analysis is possible. The progress of reaction in this case can be followed by withdrawing a small amount of reaction mixture from time to time and titrating the free acid by a standard alkali solution. Care should be taken that during the chemical analysis the reaction should not be allowed to proceed further to an appreciable extent. This can be achieved by **quenching the reaction**, which is defined as practically stopping the reaction by making some suitable alteration in the system. Generally, quenching is done by diluting the reaction mixture enormously with chilled water or sometimes by simply cooling in a ice bath. The quenching procedure is based on the fact that by lowering the temperature the rate of reaction is effectively decreased.

The concentration or the physical property which is measured to follow the course of reaction is then plotted against time. The rate of reaction at any particular instant can be determined by the slope of the tangent drawn at that point on the curve.

Factors Influencing the Reaction Rate

From experimental observations it has been found that the rates of chemical reactions can be controlled by a few factors only. The most frequently encountered factors are :

(*i*) Nature of reactants,

(*ii*) Concentrations of reactants,

(*iii*) Temperature, and

(*iv*) Catalysts.

At this place we shall discuss these factors qualitatively. This will form the background for the more specific and quantitative study later in the chapter.

(*i*) The chemical reaction occurs with the breaking of certain bonds and the formation of new bonds. The rate of reaction, therefore, depends on the specific bonds involved and hence on the nature of reactants. For example, the reduction of MnO_4^- in acid solution can be done in the following two ways :

(*a*) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

(*b*) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

The reaction (*a*) is slow and the reaction (*b*) is very fast. In these two reactions every thing is identical except the chemical nature of the reducing agent and hence it is responsible for the difference in the rates. The physical nature of reactants are also of importance in heterogeneous reactions where the rate depends on the area of the interface between the reacting substances. For example, in the combustion of wood, the rate of burning the wood in the form of log is quite different from the rate of burning of wood in the form of chips or saw dust.

(*ii*) According to the law of mass action, the greater is the concentration of reactants, the more rapidly the reaction will proceed. This is one of the fundamental concepts in the chemical reactions. We shall discuss the effect of concentration on the reaction rates in detail later in this chapter.

(*iii*) It is generally observed that *the rise in temperature increases the reaction rate.* A *quantitative relationship* between the temperature and the reaction rate will be developed later in this chapter.

(*iv*) **Catalysts** *are substances, which when added to the reaction mixture, influence the rate of reaction.* Their role is not fully understood. A very small quantity of the catalyst is required and remains unchanged chemically after the reaction has ended. For example, a pinch of MnO_2 accelerates the decomposition of $KClO_3$ into KCl and O_2 considerably and remains chemically unchanged after the reaction is over.

Apart from these factors, the nature of medium and [illegible] of radiations also influence the rates of chemical reactions.

Specific Reaction Rate

According to the law of mass action, at a given temperature the rate of a single reaction step is proportional to the product of the instantaneous molar concentrations of the reactants raised to the power given by a numeral coefficient of their respective molecules in the stoichiometric equation that describes the process. Let us take a general reaction.

$$aA+bB+cC+... \rightarrow \text{Products} \qquad ...(3{\cdot}10)$$

According to the law of mass action,

$$\text{Rate of reaction} \propto [A]^a\,[B]^b\,[C]^c...$$
$$= k[A]^a\,[B]^b\,[C]^c... \qquad ...(3{\cdot}11)$$

where k is the proportionality constant and is called by various names, such as **specific reaction rate, velocity constant, rate constant,** or **velocity coefficient.** The value of k depends on the nature of reacting substances and the temperature. Thus, at a given temperature, k is a specific characteristic constant for a reaction.

If [A], [B], [C]...are equal to unity, the specific reaction rate becomes equal to the rate of reaction. The **specific reaction rate** of a reaction may, therefore, be defined as *the rate of the reaction when the concentration of each of the reactants is unity.*

Dimensions of Reaction Rates and Specific Reaction Rates

According to Eq. (3·1),

$$\text{the rate of reaction} = \frac{dc}{dt} = \frac{\text{change in concentration}}{\text{Time taken for the change}}$$
$$= \text{Conc Time}^{-1} \qquad ...(3{\cdot}12)$$

If the concentration is expressed in moles/lit and the time in sec, then the units of rate will be

$$\text{rate} = (\text{moles/lit})\ \text{sec}^{-1}$$
$$= \text{moles lit}^{-1}\ \text{sec}^{-1}. \qquad ...(3{\cdot}13)$$

According to Eq. (3·11)

$$\text{rate of reaction} = k[A]^a\,[B]^b\,[C]^c...$$
$$\text{or conc Time}^{-1} = k(\text{conc})^a\,(\text{conc})^b\,(\text{conc})^c...$$
$$\text{or} \quad k = (\text{conc})^{1-(a+b+c...)}\ \text{Time}^{-1} \qquad ...(3{\cdot}14)$$

If the concentration is expressed in moles/lit and time in sec, then the units of specific reaction rate will be

$$k = \left(\frac{\text{moles}}{\text{litre}}\right)^{1-(a+b+c+...)} \text{sec}^{-1}$$

$$\text{or} \quad k = \left(\frac{\text{litre}}{\text{mole}}\right)^{(a+b+c+...)-1} \text{sec}^{-1} \qquad ...(3{\cdot}15)$$

The Concept of Reaction Mechanism

In the molecular view of matter, it is proposed that the molecules must collide for the reaction to occur. Thus, chemical reaction depends on the collision between the reacting particles which may be atoms, molecules, or ions. Due to these collisions, the rearrangement of atoms, electrons, and chemical bond takes place and as a result of this, new species (products) are formed. A chemical reaction may occur in one step or in a sequence of steps. For example, the reaction between hydrogen and iodine to form hydrogen iodide takes place in one step :

$$H_2+I_2 = 2HI$$

In this reaction, H_2 and I_2 molecules approach each other, collide, and form HI molecules.

On the other hand, let us consider a reaction between Fe^{2+} and $HCrO_4^-$ in acid solution. The net change is represented as

$$3Fe^{2+}+HCrO_4^-+7H^+ \rightarrow 3Fe^{3+}+Cr^{3+}+4H_2O$$

From this equation it is evident that 11 ions should collide with each other simultaneously if the reaction takes place in one step. In fact, simultaneous collision between even four particles is highly improbable so what to talk of 11 particles. The chances of such collision will be extremely low and the reaction would proceed with extremely small rate beyond measuring limits. But this reaction occurs at an easily measurable rate. This can happen only if we presume that the reaction is occurring in a sequence of simpler steps which do not involve improbable collisions. Thus, many reactions do not follow the simple path and proceed through a number of steps. Each such step is called an **elementary reaction** *or* **elementary process.** *The sequence of elementary reactions, i.e., the reaction pathway, through which the overall reaction occurs is called* a **reaction mechanism.**

One should not try to predict a simple mechanism on the basis of a simple stoichiometric equation since sometimes it is misleading. For example, the following reaction

$$H_2+Cl_2 = 2HCl$$

has simple stoichiometric equation but the kinetic study shows that this reaction is complex one and has the following mechanism :

$$Cl_2 \rightarrow 2Cl$$
$$Cl+H_2 \rightarrow HCl+H$$
$$H+Cl_2 \rightarrow HCl+Cl$$

The reaction involves the repetition of some elementary processes and hence follows the **chain mechanism.**

When a chemical change occurs through a sequence of [illegible] having different rates, the slowest step controls the rate of o[illegible]

eaction, and is called the **rate-determining step.** For example, he oxidation of gaseous hydrogen bromide at about 500°C is supposed to occur in three steps

$$(i)\quad HBr + O_2 \rightarrow HOOBr \qquad ...slow$$

$$(ii)\quad HOOBr + HBr \rightarrow 2HOBr \qquad ...fast$$

$$(iii)\quad HOBr + HBr \rightarrow H_2O + Br_2] \times 2 \qquad ...fast$$

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$

The reaction (*i*) being slow is the rate determining step. It is also confirmed by the fact that equal changes in the partial pressures of HBr and O_2 produce the same effect on the rate.

Similarly, the decomposition of N_2O_5 occurs in three steps :

$$(i)\quad N_2O_5 \rightarrow N_2O_3 + O_2 \qquad ...slow \qquad ...(3{\cdot}16)$$

$$(ii)\quad N_2O_3 \rightarrow NO + NO_2 \qquad ...fast$$

$$(iii)\quad NO + N_2O_5 \rightarrow 3NO_2 \qquad ...fast$$

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \qquad ...(3.17)$$

The reaction (*i*) being slow is the rate determining step.

When the stoichiometric equation for the overall reactions does not represent the correct nature of chemical process, the rate equation should be formed by applying the law of mass action to the rate determining step instead of the overall stoichiometric equation. For example, in case of decomposition of N_2O_5, if the law of mass action is applied to Eq. (3·17) then,

$$\text{The rate of reaction} = k\,[N_2O_5]^2$$

which is not correct. The correct rate expression can be written by applying the law of mass action to Eq. (3·16), which is the rate determining step *i.e.*,

$$\text{The rate of reaction} = k\,[N_2O_5]$$

Reaction Order

The order of a reaction is purely an experimental quantity. We can determine the rate experimentally and find how the rate depends on the change of concentrations of individual reactants. The relationship between the experimentally measured rate of reaction and the concentrations of the reactants can be shown by an equation called the **differential rate equation** or the **rate equation.** Thus, if the rate of a reaction is proportional to the first power of the concentration of one reactant, then the rate equation is

$$\text{rate} = kc$$

such a reaction is said to be of **first order.** For example, the decomposition of N_2O_5 is the first order reaction. The experimental

rate of this reaction is proportional to the first power of the concentration of N_2O_5, *i.e.*,

$$\text{rate} = kc_{N_2O_5}$$

The **second order** reactions are of two types :

(*i*) The reactions in which the rate of reaction is proportional to the square of concentration of one reactant *i.e.*,

$$\text{rate} = kc^2$$

For example, the decomposition of hydrogen iodide

$$2HI \rightarrow H_2+I_2$$

is the reaction of second order because the rate equation is

$$\text{rate} = kc^2_{HI}$$

(*ii*) The reactions in which the rate is proportional to the product of the first power of the concentrations of two different reactants, *i.e.*,

$$\text{rate} = kc_A c_B.$$

For example, the formation of hydrogen iodide from hydrgen and iodine

$$H_2+I_2 \rightarrow 2HI$$

is of second order because the rate equation is

$$\text{rate} = kc_{H_2}\, c_{I_2}$$

This reaction is in fact first order with respect to hydrogen and first order with respect to iodine.

Similarly, **third order** reactions are those in which the rate is proportional to the three exponents of the concentration terms. For example, the reaction between nitric oxide and oxygen,

$$2NO+O_2 \rightarrow 2NO_2$$

is of third order because the rate equation is found to be

$$\text{rate}=kc^2_{NO}c_{O_2}$$

The rate is proportional to square of the nitric oxide conce[illegible] and to the first power of the oxygen concentration. Th[illegible] reaction is second order with respect to nitric oxide and [illegible] with respect to oxygen. The overall order of this reac[illegible]

Thus, for a general reaction

$$aA+bB+cC+\ldots \rightarrow \text{Products}$$

if it is found *experimentally* that the rate is [illegible] power of the concentration of A, b th power of [illegible] c th power of the concentration C and so on. [illegible] is

$$\text{rate} = kc_A^a\, c_B^b$$

which shows that the reaction is a th order with respect to A, b th order with respect to B, c th order with respect to C and so on. The overall order of the reaction n, is given by

$$n = a+b+c+...$$

Thus, the **order of reaction** may be defined as *sum of the powers to which the concentration terms are raised in the experimentally determined rate equation for the reaction.*

The order of a reaction should not be predicted from the stoichiometric equation for the reaction but the order with respect to each reactant must be determined *experimentally.* For example, the decomposition of N_2O_5 and NO_2 have the following stoichiometric equations of similar form :

$$2N_2O_5 \rightarrow 4NO_2+O_2$$
$$2NO_2 \rightarrow 2NO + O_2$$

But the experimental determination shown that the first reaction is of first order and the other is of second order. Also, in case of the following reactions :

$$CH_3CHO \rightarrow CH_4 + CO$$
$$3KClO \rightarrow KClO_3 + 2KCl$$

if we deduce the order from the stoichiometric equations, the first reaction appears to be of first order and the second one of the third order. But actual experimental determinations show that both the reactions are of second order. Thus, we see that the prediction of the order of reaction from the stoichiometric equation may lead to wrong conclusions.

The order of reaction is not necessarily a whole number, it may be fractional or zero also. For example, the thermal conversion of *para* hydrogen into *ortho* hydrogen is a reaction of the order of 3/2. The rate expression is

$$\text{rate} = k[p\text{-}H_2]^{3/2}$$

Such fractional order reactions are of complex nature.

The order of reaction can be changed by changing the experimental conditions.

Molecularity of a Reaction

The concept of molecularity of a reaction is used to show the molecular mechanism by which the reaction occurs. The term **molecularity** is used to describe the individual elementary reaction and is defined as *the number of molecules, atoms, or radicals that must collide simultaneously in order for the reaction to take place* or in other words it refers to *the number of molecules, atoms or radicals taking part in an elementary reaction.* Thus, the reaction may be called unimolecular, bimolecular, termolecular etc., depending upon whether one, two, three or more molecules, are participating in the elementary process. As already discussed, since the simul-

taneous collisions of four or more molecules are highly improbable, the elementary reactions of higher molecularity are very rare.

In general, for *elementary processes*, the order and the molecularity are the same. Thus, a unimolecular reaction is of first order, a bimolecular reaction is of second order, and a termolecular reaction is of third order, but it is not always true. Let us take following reaction

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Suppose one of the reactants, say water, is present in large excess so that its concentration does not change appreciably during the course of reaction. Then the rate equation will not involve this concentration term and rate will be proportional to the first power of the concentration of ethyl acetate. Thus, the order of this reaction will be *one*, but since two molecules are reacting in this elementary reaction, the molecularity will be two. Such a reaction is called **pseudo unimolecular reaction.**

If the reaction is complex one and involves a number of elementary steps, it is meaningless to speak of the molecularity of the overall reaction because one elementary step may involve two molecules and another may involve only one molecule.

One should have a clear distinction between the **order** and the **molecularity.** The order is an experimental quantity and expresses the dependence of the reaction rate on the concentrations of the reacting substances while the molecularity applies to the theoretical mechanism showing the number of molecules involving in an elementary reaction. The molecularity refers to each elementary step in a chemical reaction while the order is related to the whole observable reaction. Further, the order may be integral, fractional or zero but the molecularity is always a positive integer and is never zero.

Homogeneous and Heterogeneous Reactions

From the kinetic point of view, the reactions are [illegible] two classes, *viz.* **homogeneous reactions,** and **[illegible] reactions. Homogeneous reactions** *are those* [illegible] *occur entirely in one phase, i.e.,* either in the gas phase [illegible] **Heterogeneous reactions** *are those which occur* [illegible] *between two phases.* Reactions taking place at [illegible] catalyst or on the walls of the container, are heterogen[illegible]

This chapter is devoted to the kinetics of [illegible] as the kinetics of heterogeneous reactions is [illegible] book. Now, we shall study the quantitative [illegible] kinetics of homogeneous reactions from [illegible] order.

First-Order Reactions

A **first order reaction** is defined as *one in which the rate of the reaction is proportional to the first power of the concentration of the reactant.*

A general reaction of the first order can be represented as

$$A \rightarrow \text{Products.}$$

The differential rate equation for this reaction is

$$\frac{-dc_A}{dt}=k_1c_A \qquad ...(3\cdot18)$$

where c_A is the concentration of reactant A at any time t and k_1 is the specific reaction rate of the first order reaction.

Let a moles/litre be the initial concentration of A. Suppose x moles/litre of it have been decomposed upto the time t. Hence, at time t, the concentration of A, *i.e.*, $c_A=(a-x)$. Putting this value in Eq. (3·18), we get

$$\frac{-d(a-x)}{dt}= k_1 (a-x)$$

or
$$\frac{dx}{dt} = k_1(a-x) \qquad ...(3\cdot19)$$

or
$$\frac{dx}{(a-x)}= k_1dt \qquad ...(3\cdot20)$$

Knowing the fact that at the start of the reaction $t=0$ and $x=0$ and when $t=t$, $x=x$, we can integrate Eq. (3·20) within these limits and obtain

$$\int_{x=0}^{x=x} \frac{dx}{a-x} = \int_{t=0}^{t=t} k_1dt$$

or
$$\left[-\ln (a-x) \right]_{x=0}^{x=x} = \left[k_1t \right]_{t=0}^{t=t}$$

or
$$-\ln (a-x)+\ln a = k_1t$$

or
$$\ln \frac{a}{a-x} = k_1t \qquad ...(3\cdot21)$$

or
$$2\cdot303 \log_{10}\frac{a}{a-x}=k_1t \qquad ...(3\cdot22)$$

or
$$k_1 = \frac{2\cdot303}{t} \log_{10}\frac{a}{a-x} \qquad ...(3\cdot23)$$

This is the **integrated rate equation*** for the first order reaction and is commonly known as **kinetic equation** for the first order reaction. Other forms of the equation are as follows :

(*i*) **Wilhelmy's equation for the first order reaction.** Eq·

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*The integrated rate equation shows the dependence of the reactant concentration on time, whereas the differential rate equation shows the dependence of rate of reaction on the concentration of the reactant.

(3·23) can be written in another form. Let c_o be the initial concentration of the reactant and c_t be the concentration at any time t, then $a = c_o$ and $a - x = c_t$. Substituting these values in Eq. (3·21), we obtain

$$\ln \frac{c_o}{c_t} = k_1 t$$

$$\ln \frac{c_t}{c_o} = -k_1 t$$

or $$\frac{c_t}{c_o} = e^{-k_1 t}$$

or $$c_t = c_o e^{-k_1 t} \qquad ...(3·24)$$

This is known as **Wilhelmy's equation.**

(*ii*) **Interval Formula.** If the initial concentration of A is not known then the interval formula can be used to calculate the rate constant k_1. The initial concentration of the reactant is eliminated in this formula. Let x_1 and x_2 be the amounts decomposed upto the time t_1 and t_2 respectively. Using Eq. (3·22), we can write

$$t_1 = \frac{2·303}{k_1} \log_{10} \frac{a}{a-x_1} \qquad ...(3·25)$$

and $$t_2 = \frac{2·303}{k_1} \log_{10} \frac{a}{a-x_2} \qquad ...(3·26)$$

Subtracting Eq. (3·25) from Eq. (3·26), we get

$$t_2 - t_1 = \frac{2·303}{k_1}\left(\log_{10} \frac{a}{a-x_2} - \log_{10} \frac{a}{a-x_1}\right)$$

or $$t_2 - t_1 = \frac{2·303}{k_1} \log_{10} \frac{a-x_1}{a-x_2} \qquad ...(3·27)$$

or $$k_1 = \frac{2·303}{t_2 - t_1} \log_{10} \frac{a-x_1}{a-x_2} = \frac{2·303}{t_2 - t_1} \log_{10} \frac{c_1}{c_2} \qquad ...(3·28)$$

where c_1 and c_2 are the concentrations of the reactants at times t_1 and t_2 respectively.

Graphical representation of a First-order Reaction

From Eq. (3·23), we can write

$$t = \frac{2·303}{k_1} \log_{10} \frac{a}{a-x} \qquad ...(3·$$

This equation shows that when $\log_{10} \frac{a}{a-x}$ is plotted

a straight line passing through the origin is obtained. Th positive as shown in Fig. 3·4 (*a*). Eq. (3·29) can a as :

$$t = -\frac{2·303}{k_1} \log_{10}(a-x) + \frac{2·303}{k_1} \log_{10} a$$

This equation shows that when $\log_{10}(a-x)$ is plotted against t, a straight line with negative slope is obtained as shown in Fig 3·4 (*b*).

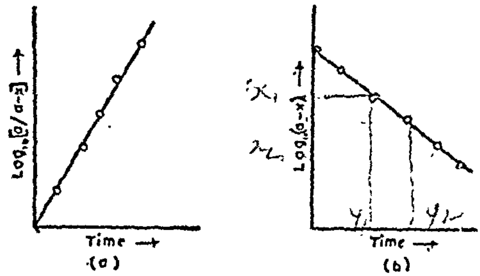


Fig 3·4. Graphical Representation of a First-order Reaction.

A straight line may be obtained if $\log_{10}\dfrac{a-x_1}{a-x_2}$ is plotted against t_2-t_1 as is evident from Eq. (3·27).

Half life Period of First-order Reactions ($t_{\frac{1}{2}}$). *It is the time required for the decomposition of half of the original substance.* Thus, if $t=t_{\frac{1}{2}}$ then $x=a/2$. Putting these values in Eq. (3·29), we get

$$t_{\frac{1}{2}} = \frac{2\cdot303}{k_1}\log_{10}\frac{a}{a-a/2} = \frac{2\cdot303}{k_1}\log_{10}2$$

$= \frac{2\cdot303}{K_1}\log_{10}\frac{a}{a}$

$= 2\cdot303$ l

or $$t_{\frac{1}{2}} = \frac{0\cdot693}{k_1} \qquad \ldots(3\cdot31)$$

Eq. (3·31) shows that the **half life period of a first order reaction** *is independent of the initial concentration.* This is true for the decomposition of *any fraction* of the change. for example, if $t_{\frac{3}{4}}$ is the time required to decompose 3/4th of the original concentration of the reactant, then when $t=t_{\frac{3}{4}}$, $x=3/4\,a$. Putting these values in Eq. (3·29), we get

$$t_{\frac{3}{4}} = \frac{2\cdot303}{k_1}\log\frac{a}{a-\frac{3}{4}a} = \frac{2\cdot303}{k_1}\log 4 \qquad \ldots(3\cdot32)$$

which shows that $t_{\frac{3}{4}}$ is independent of initial concentrations.

Hence, we can generalize that in **first order reactions** *the time required to decompose any definite fraction of the initial concentration is independent of the initial concentration.*

Units of k_1. The dimension of k_1 can be obtained by putting $a+b+c+\ldots=1$ in Eq. (3·14). Thus,

$$k_1 = \text{Time}^{-1} \qquad \ldots(3\cdot33)$$

The units generally used are sec^{-1}, min^{-1} and $hour^{-1}$. Since Eq. (3·33) contains no concentration terms, the change in the concentration units will have no effect on the value of k_1.

Summary of the characteristics of First-order Reactions

(i) Differential rate equation : $\frac{dx}{dt}=k_1\,(a-x)$

(ii) Integrated rate equations : $k_1=\frac{2\cdot303}{t}\log_{10}\frac{a}{a-x}$

$$c_t=c_0e^{-k_1t}$$

$$t_2-t_1=\frac{2\cdot303}{k_1}\log_{10}\frac{a-x_1}{a-x_2}$$

(iii) Graphical representation : The plots—(a) $\log_{10}\frac{a}{a-x}$ vs. t, (b) $\log_{10}(a-x)$ vs t, (c) $\log_{10}\frac{a-x_1}{a-x_2}$ vs. (t_2-t_1) give straight lines.

(iv) The half-life period or the time required to decompose any fraction of the initial concentration of the reactant is independent of its initial concentration.

(v) k_1 has dimensions of Time^{-1} and the change in concentration units has no effect on the value of k_1.

Example 1. *The rate constant of a first order reaction is $6\cdot2\times10^{-4}\ sec^{-1}$. Calculate the rate of the reaction in (i) mole lit^{-1} sec^{-1}, (ii) mole lit^{-1} min^{-1}, (iii) mole cc^{-1} min^{-1} and (iv) mole cc^{-1} sec^{-1} when the initial concentration of the reactant is 0·4 mole lit^{-1}.*

Solution. (i) We know that

rate $=k_1c$

Here $k_1=6\cdot2\times10^{-4}\ sec^{-1}$

and $c=0\cdot4$ moles lit^{-1}

$\therefore$ rate $=6\cdot2\times10^{-4}\times0\cdot4$

$=2\cdot48\times10^{-4}$ mole lit^{-1} sec^{-1}.

(ii) *rate in mole lit^{-1} min^{-1}*

Since 1 min $=60$ sec

or $1\ sec^{-1}=60\ min^{-1}$

$\therefore$ rate $=2\cdot48\times10^{-4}\times60$

$=1\cdot488\times10^{-2}$ mole lit^{-1} min^{-1}.

(iii) *rate in mole cc^{-1} min^{-1}*

Since 1 litre $=1000$ c.c.

or $1\ lit^{-1}=\frac{1}{1000}\ cc^{-1}$

$\therefore$ rate $=1\cdot488\times10^{-2}\times\frac{1}{1000}$

$=14\cdot88\times10^{-6}$ mole cc^{-1} min^{-1}.

(iv) *rate in mole cc^{-1} sec^{-1}*

rate $=2\cdot48\times10^{-4}\times\cancel{1000}\ \frac{1}{1000}$

$=0\cdot248\times10^{-6}$ mole cc^{-1} sec^{-1}.

Example 2. *A first order reaction is 40% complete in 50 inutes. Calculate the value of its rate constant in hour*$^{-1}$. *What the percentage of the reactant that would remain unchanged at e end of 2·5 hours ?*

Solution. We know that

$$k_1 = \frac{2{\cdot}303}{t}\log_{10}\frac{a}{a-x}$$

Here $t = 50 \text{ min} = \frac{50}{60}\text{ hour}$

$$x = 0{\cdot}4\,a$$

$$\therefore \quad k_1 = \frac{2{\cdot}303}{50/60}\log_{10}\frac{a}{a-0{\cdot}4a}$$

$$= \frac{2{\cdot}303\times 60}{50}\log_{10}\frac{1}{0{\cdot}6} = 0{\cdot}6120 \text{ hour}^{-1}$$

In the second case

$$k_1 = 0{\cdot}612 \text{ hour}^{-1}$$

$$t = 2{\cdot}5 \text{ hours}$$

$$\therefore \quad 0{\cdot}612 = \frac{2{\cdot}303}{2{\cdot}5}\log_{10}\frac{a}{a-x}$$

$$\text{or } \log_{10}\frac{a}{a-x} = \frac{0{\cdot}612\times 2{\cdot}5}{2{\cdot}303} = 0{\cdot}6649$$

$$\text{or} \quad \frac{a}{a-x} = 4{\cdot}623$$

The fraction left unchanged after 2·5 hours is

$$\frac{a-x}{a} = \frac{1}{4{\cdot}625} = 0{\cdot}2163$$

∴ Percentage of the reactant left unchanged after 2·5 hours

$$= 21{\cdot}63\%.$$

Examples of First-order Reactions

(*a*) **Gaseous Reactions.** There are numerous examples of homogeneous gas-phase first order reactions such as thermal decomposition of nitrogen pentoxide, acetone, azomethane, azoisopropane, ethyl amine, paraldehyde, ethyl bromide, nitrous oxide etc. We shall take the following example in detail :

Thermal decomposition of azoisopropane. The decomposition of azoisopropane into nitrogen and hexane, takes place according to the equation

$$(CH_3)_2CHN{=}NCH\,(CH_3)_2 \rightarrow N_2 + C_6H_{14}$$

The progress of the reaction can be followed by measuring the pressure at different time intervals. Let P_0 be the initial pressure of azoisopropane and P be the total pressure of the reaction mixture at any time t. Suppose, at time t, the partial pressure

of azoisopropane, nitrogen, and hexane are p_A, p_{N_2} and $p_{C_6H_{14}}$ respectively, and the decrease in the pressure of azoisopropane is x. Then,

$$p_{N_2} = p_{C_6H_{14}} = x \qquad ...(i)$$

and

$$p_A = P_o - x \qquad ...(ii)$$

The total pressure of the system is given by

$$\begin{aligned} P &= p_A + p_{N_2} + p_{C_6H_{14}} \\ &= P_o - x + x + x \\ &= P_o + x \end{aligned}$$

or

$$x = (P - P_o)$$

Substituting this value of x in Eq. (ii), we get

$$p_A = P_o - P + P_o = (2P_o - P) \qquad ...(iii)$$

Since P_o is the intitial pressure of azoisopropane, it is proportional to a in the Eq. (3·23), and p_A at time t is proportional to $(a-x)$, hence we can write

$$k_1 = \frac{2 \cdot 303}{t} \log_{10} \frac{P_o}{p_A}$$

Putting the value of p_A from Eq. (iii), we get

$$k_1 = \frac{2 \cdot 303}{t} \log_{10} \frac{P_o}{(2P_o - P)}$$

Example 3. *The following data were obtained for the decomposition of azoisopropane at 270°C.*

Time (min)	*0*	*3*	*6*	*9*	*12*
Pressure (mm Hg)	*35·15*	*46·3*	*53·9*	*58·85*	*62·2*

Show that the reaction is of first order.

Solution. The reaction will be of the first-order if the values of the velocity constant obtained by the following equation show a fair degree of constancy :

$$k_1 = \frac{2 \cdot 303}{t} \log_{10} \frac{P_o}{(2P_o - P)}$$

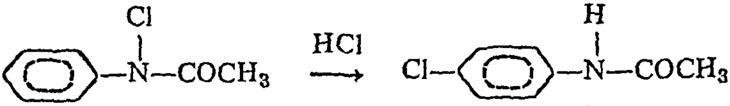
Here P_o = 35·15 mm Hg.

t (min)	$2P_o - P$ (mm Hg)	$\frac{2 \cdot 303}{t} \log_{10} \frac{P_o}{(2P_o - P)} = k_1$ min^{-1}
3	70·3—46·3=24·0	$\frac{2 \cdot 303}{3} \log_{10} \frac{35 \cdot 15}{24} = 0 \cdot 1272$ min^{-1}
6	70·3—53·9=16·4	$\frac{2 \cdot 303}{6} \log_{10} \frac{35 \cdot 15}{16 \cdot 4} = 0 \cdot 1266$ min^{-1}
9	70·3—58·85=11·45	$\frac{2 \cdot 303}{9} \log_{10} \frac{35 \cdot 15}{11 \cdot 45} = 0 \cdot 1242$ min^{-1}
12	70·3—62·2=8·1	$\frac{2 \cdot 303}{12} \log_{10} \frac{35 \cdot 15}{8 \cdot 1} = 0 \cdot 1218$ min^{-1}

A fair constancy in the value of k_1 shows that the reaction is of the first order.

(*b*) **Reactions in Solution.** Out of a number of first-order reactions in solutions we shall describe the following reactions only :

(1) **Conversion of N-chloracetanilide into *p*-chloracetanilide.** This isomeric change takes place in presence of HCl which acts as a catalyst.



N-chloracetanilide p-chloracetanilide

This reaction is of first-order. The progress of the reaction can be followed by withdrawing a definite quantity of reaction mixture different time intervals, adding to excess of KI solution, and titrat at ing the liberated iodine with standard hypo solution. The iodine is liberated according to the following reaction :

$$C_6H_5NClCOCH_3+2KI \longrightarrow C_6H_5NH\ COCH_3+HCl+I_2$$

N-chloracetanilide liberates iodine from the KI solution while *p*-chloracetanilide remaining unaffected. Thus, the volume of hypo solution used in titration at any time *t*, corresponds to the amount of unchanged N-chloracetanilide at that time.

Example 4. *From the following data, show that the conversion of N-chloracetanilide into p-chloracetanilide is a first-order reaction :*

Time (hours)	*0*	*1*	*2*	*3*	*4*
N	*20*	*14·4*	*10·4*	*7·4*	*5·6*

where N is the number of ml of hypo solution required for titrating 5 ml of the solution mixture in excess of KI solution at different time intervals.

Solution. We know that the kinetic equation for the first order reaction is

$$k_1=\frac{2\cdot303}{t}\log_{10}\frac{a}{a-x}$$

Here, the volume of hypo solution corresponds to the amount of N-chloracetanilide present, hence *a* may be taken equal to 20 ml and (*a*—*x* , at different times, may be taken equal to 14·4, 10·4, 7·4 and 5·6 ml.

Substituting these values in the above equation, we get

$$k_1=\frac{2\cdot303}{1}\log_{10}\frac{20}{14\cdot4}=0\cdot3285\ \text{min}^{-1}$$

$$k_1=\frac{2\cdot303}{2}\log_{10}\frac{20}{10\cdot4}=0\cdot3271\ \text{min}^{-1}$$

$$k_1=\frac{2\cdot303}{3}\log_{10}\frac{20}{7\cdot4}=0\cdot3315\ \text{min}^{-1}$$

$$k_1=\frac{2\cdot303}{4}\log_{10}\frac{20}{5\cdot6}=0\cdot3182\ \text{min}^{-1}$$

A fair constancy in the values of k_1 shows that the reaction is of first-order.

2. Inversion of cane sugar. Wilhelmy, *for the first time* studied the rate of inversion of cane sugar in presence of dilute acids which act as catalyst. The equation for the reaction is

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{dil HCl}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The solution of sucrose is dextro-rotatory and its specific rotation is $+66{\cdot}5°$. On hydrolysis, in presence of dil. HCl, it gives a mixture of equal amounts of glucose and fructose. Glucose is dextro-rotatory with specific rotation of $+52{\cdot}7°$ and fructose is laevo rotatory with specific rotation of $-92{\cdot}4°$. The mixture of equal concentrations of glucose and fructose in thus laevo-rotatory. This process in known as **inversion of cane sugar** because the optical property is inverted *i.e.*, dextro behaviour changes to leavo behaviour.

The progress of the reaction can be followed by measuring the change in the rotation of the plane of polarisation of polarised light by means of a polarimeter. The change in the angle of rotation is proportional to the amount of sugar inverted.

Suppose the initial reading of the polarimeter is θ_o, the final reading Is θ_∞ and the reading at any time t is θ_t, as shown in Fig. 3·5. The total change in the angle of rotation at the end of the experiment, *i.e.*, $(\theta_o - \theta_\infty)$ will be proportional to a, the initial concentration of cane sugar, and $(\theta_t - \theta_\infty)$ will be proportional to $(a-x)$, the amount of unchanged sugar. Hence

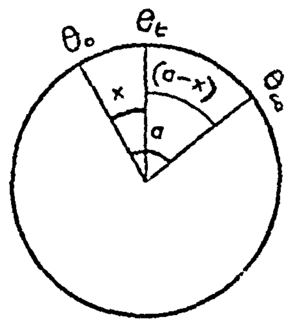


Fig. 3·5.
Polarimeter Readings

$$k_1 = \frac{2.303}{t}\log_{10}\frac{a}{a-x} = \frac{2{\cdot}303}{t}\log_{10}\frac{\theta_o - \theta_\infty}{\theta_t - \theta_\infty}$$

Example 5. *The optical rotations of sucrose in presence of dilute HCl at various times are given below :*

Time (min)	*0*	*20*	*40*	*60*	*80*	∞
Rotation (degress)	*+13·0*	*+9·95*	*+7·45*	*+5·4*	*+3·7*	—

show that the reaction is of first-order.

Solution. We know that

$$k_1 = \frac{2{\cdot}303}{t}\log_{10}\frac{\theta_o - \theta_\infty}{\theta_t - \theta_\infty}$$

Here $\theta_o - \theta_\infty = [13{\cdot}0 - (-4{\cdot}0)] = 17{\cdot}0.$

The value of k_1 at different given times in calculated as under :

Time (min)	$\theta_t - \theta_\infty$ (degrees)	$\frac{2 \cdot 303}{t} \log_{10} \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} = k_1$ (min⁻¹)
20	$9 \cdot 95-(-4 \cdot 0)=13 \cdot 95$	$\frac{2 \cdot 303}{20} \log_{10} \frac{17}{13 \cdot 95}=9 \cdot 881 \times 10^{-3}$
40	$7 \cdot 45-(-4 \cdot 0)=11 \cdot 45$	$\frac{2 \cdot 303}{40} \log_{10} \frac{17}{11 \cdot 45}=9 \cdot 874 \times 10^{-3}$
60	$5 \cdot 4-(-4 \cdot 0)= 9 \cdot 4$	$\frac{2 \cdot 303}{60} \log_{10} \frac{17}{9 \cdot 4}=9 \cdot 874 \times 10^{-3}$
80	$3 \cdot 7-(-4 \cdot 0)= 7 \cdot 7$	$\frac{2 \cdot 303}{80} \log_{10} \frac{17}{7 \cdot 7}=9 \cdot 900 \times 10^{-3}$

A fair constancy in the values of k_1 shows that the inversion of sucrose is of first-order.

3. Hydrolysis of an Ester. The hydrolysis of an ester, *e.g.*, ethyl acetate catalysed by H^+ ions, takes place according to the equation

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

As already discussed this reaction is of first-order because water is present in large excess. The progress of the reaction can be followed by withdrawing a definite amount of the reaction mixture at different times, quenching, and estimating the free acid liberated by titrating against standarnd alkali. The final reading is taken after 24 hours when it is supposed that the reaction is over. Let V_o, V_t, and V_∞ be the volumes of standard alkali used for a definite quantity of reaction mixture at the commencement of the reaction, at any time t, and at the end of reaction respectively. Then $(V_\infty - V_o)$ will correspond to the initial concentration a and $(V_\infty - V_t)$ will correspoud to $(a-x)$ at time t. Hence

$$k_1 = \frac{2 \cdot 303}{t} \log_{10} \frac{V_\infty - V_o}{V_\infty - V_t}$$

Example 6. *Ethyl acetate was subjected to hydrolysis in excess of dil. HCl at 25°C. 5 cc of reaction mixture was withdrawn at different interval of time and, after quenching, titrated with standard NaOH solution. The following results were obtained :*

Time (min)	*0*	*40*	*80*	*120*	*160*	∞
Volume of NaOH (ml)	*18·5*	*20·7*	*22·6*	*24·2*	*25·6*	*34·8*

Show that the reaction is of first-order.

Solution. The reaction will be of first-order if the values of k_1 at different times, obtained by the following equation show constancy.

$$k_1 = \frac{2 \cdot 303}{t} \log_{10} \frac{V_\infty - V_o}{V_\infty - V_t}$$

Here $V_\infty - V_o = 34 \cdot 8 - 18 \cdot 5 = 16 \cdot 3$ ml.

The values of k_1 at different given times are calculated as under :

t (min)	$V_\infty - V_t$ (ml)	$\frac{2\cdot303}{t}\log_{10}\frac{V_\infty - V_0}{V_\infty - V_t}$ =	k_1 (min^{-1})
40	34·8—20·7 = 14·1	$\frac{2\cdot303}{40}\log_{10}\frac{16\cdot3}{14\cdot1}$	$= 3\cdot626\times10^{-3}$
80	34·8—22·6 = 12·2	$\frac{2\cdot303}{80}\log_{10}\frac{16\cdot3}{12\cdot2}$	$= 3\cdot621\times10^{-3}$
120	34·8—24·2 = 10·6	$\frac{2\cdot303}{120}\log_{10}\frac{16\cdot3}{10\cdot6}$	$= 3\cdot587\times10^{-3}$
160	34·8—25·6 = 9·2	$\frac{2\cdot303}{160}\log_{10}\frac{16\cdot3}{9\cdot2}$	$= 3\cdot576\times10^{-3}$

A fair constancy in the value of k_1 shows that the reaction is of first-order.

4. Decomposition of H_2O_2 in aqueous solution. In presence of finely divided platinum, hydrogen peroxide decomposes in aqueous solution according to the following equation :

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

The progress of the reaction can be followed by any of the following methods :

(*i*) By measuring the volume of O_2 evolved at different intervals, or

(*ii*) By withdrawing a definite amount of reaction mixture at different intervals and estimating the amount of undecomposed hydrogen peroxide by titrating with standard $KMnO_4$ solution.

The second method being convenient is usually used in the laboratory.

Example 7. *The decomposition of hydrogen peroxide was studied by titrating a definite volume of reaction mixture, at different intervals, with $KMnO_4$ and the following data were obtained :*

Time (min)	*0*	*10*	*20*	*30*	*40*
Volume of $KMnO_4$ (ml)	*12.5*	*9.9*	*7.8*	*6.1*	*4.8*

Show that the reaction is of first order and determine its rate constant.

Solution The reaction will be of the first-order if the values of k_1 obtained by the following equation are fairly constant :

$$k_1 = \frac{2\cdot303}{t}\log_{10}\frac{a}{a-x}.$$

Here, the volume of $KMnO_4$ solution used at any time corresponds to the concentration of undecomposed H_2O_2. Hence, the volume of $KMnO_4$ used at $t=0$ corresponds to the initial concentration a and at time t corresponds to $(a-x)$. Putting these values in the above equation, we get

$$k_1 = \frac{2\cdot303}{10}\log_{10}\frac{12\cdot5}{9\cdot9} \quad 2\cdot407\times10^{-2}\,\text{min}^{-1}$$

$$k_1 = \frac{2{\cdot}303}{20}\log_{10}\frac{12{\cdot}5}{7{\cdot}8} = 2{\cdot}405\times10^{-2}\text{min}^{-1}$$

$$k_1 = \frac{2{\cdot}303}{30}\log_{10}\frac{12{\cdot}5}{6{\cdot}1} = 2{\cdot}394\times10^{-2}\text{min}^{-1}$$

$$k_1 = \frac{2{\cdot}303}{40}\log_{10}\frac{12{\cdot}5}{4{\cdot}8} = 2{\cdot}398\times10^{-2}\text{min}^{-1}$$

A fair constancy in the values of k_1 shows that the reaction is of first-order.

$$\text{The average value of } k_1 = \frac{(2{\cdot}407+2{\cdot}405+2{\cdot}394+2{\cdot}398)\times10^{-2}}{4}$$

$$= 2{\cdot}401\times10^{-2}\text{min}^{-1}$$

5. Decomposition of NH_4NO_2 in aqueous solution. On warming, the aqueous solution of ammonium nitrite decomposes according to the following equation :

$$NH_4NO_2 \longrightarrow 2H_2O+N_2$$

The progress of the reaction can be followed by measuring the volume of nitrogen gas evolved at different time intervals. Suppose, V_t is the volume of N_2 evolved at any time t and V_∞ is the total volume of N_2 evolved when the reaction is over, then V_∞ corresponds to the initial concentration a and $(V_\infty - V_t)$ corresponds to the concentration $(a-x)$ at time t. Hence, we can write

$$k_1 = \frac{2{\cdot}303}{t}\log_{10}\frac{V_\infty}{V_\infty - V_t}.$$

Example 8. *From the following data show that the decomposition of ammonium nitrite in aqueous solution is a first-order reaction :*

Time (min)	*10*	*20*	*30*	*40*	∞
Volume of N_2 (ml)	*12.5*	*22.8*	*31.2*	*38 2*	*70.1*

Solution. The reaction will be of the first-order if the values of k_1 obtained by the following equation are fairly constant :

$$k_1 = \frac{2{\cdot}303}{t}\log_{10}\frac{V_\infty}{V_\infty - V_t}.$$

Here $V_\infty = 70{\cdot}1$ ml

The values of k_1 at different given times are calculated as under :

Time (min)	$V_\infty - V_t$ (ml)	$\frac{2{\cdot}303}{t}\log_{10}\frac{V_\infty}{V_\infty - V_t} = k_1$ (min^{-1})
10	$70{\cdot}1-12{\cdot}5=57{\cdot}6$	$\frac{2{\cdot}303}{10}\log_{10}\frac{70{\cdot}1}{57{\cdot}6} = 1{\cdot}964\times10^{-2}$
20	$70{\cdot}1-22{\cdot}8=47{\cdot}3$	$\frac{2{\cdot}303}{20}\log_{10}\frac{70{\cdot}1}{47{\cdot}3} = 1{\cdot}966\times10^{-2}$

30	$70{\cdot}1-31{\cdot}2=38{\cdot}9$	$\frac{2{\cdot}303}{30}\log_{10}\frac{70{\cdot}1}{38{\cdot}9}=1{\cdot}963\times10^{-2}$
40	$70{\cdot}1-38{\cdot}2=31{\cdot}9$	$\frac{2{\cdot}303}{40}\log_{10}\frac{70{\cdot}1}{31{\cdot}9}=1{\cdot}968\times10^{-2}$

A fair constancy in the values of k_1 shows that this reaction is of first-order.

We have discussed quite a good number of examples of first-order reactions in gas-phase and in solutions. The following category of reactions is also of first order.

Disintegration of Radioactive elements. The radioactive disintegration is also of first-order. For a radioactive change

$$A \longrightarrow \text{Products}$$

the specific reaction rate is given by

$$k_1=\frac{2{\cdot}303}{t}\log_{10}\frac{N_o}{N_t}$$

where N_o and N_t are the number of radioactive nuclei at the beginning and at any time t respectively. The course of change can be followed by measuring the radioactivity of the substance at different intervals of time.

Second-order Reactions

A reaction is said to be of **second-order** *if its rate depends on the square of concentrations of one substance or to the product of first power of concentration of two substances.* The possible general reactions of second order can be represented as

$$A+A \longrightarrow \text{Products} \quad ...(3{\cdot}34)$$

$$A+B \longrightarrow \text{Products} \quad ...(3{\cdot}35)$$

There exists two possibilities :

(*i*) *When a reaction involves a single substance only or involves two different substances with equal initial concentrations.*

Suppose a moles lit^{-1} is the initial concentration of A in reaction (3·34) or A and B each in reaction (3·35). At any time t, let x, moles lit^{-1} have been converted into products. The differential rate equation is given by

$$\frac{dx}{dt}=k_2(a-x)(a-x)=k_2(a-x)^2 \quad ...(3{\cdot}36)$$

where k_2 is the specific reaction rate for the second-order reaction. On rearranging Eq. (3·36), we get

$$\frac{dx}{(a-x)^2}=k_2dt \quad ...(3{\cdot}37)$$

Knowing the fact that at the start of the reaction $t=0$ and $x=0$ and at any time t, *i.e.*, when $t=t$, $x=x$, we can integrate Eq. (3·37) within these limits and obtain

$$\int_{x=0}^{x=x} \frac{dx}{(a-x)^2} = \int_{t=0}^{t=t} k_2 dt$$

or $$\left[\frac{1}{a-x}\right]_{x=0}^{x=x} = \left[k_2 t\right]_{t=0}^{t=t}$$

or $$\frac{1}{a-x} - \frac{1}{a} = k_2 t \qquad \ldots(3\cdot38)$$

or $$t = \frac{1}{k_2(a-x)} - \frac{1}{k_2 a} \qquad \ldots(3\cdot39)$$

$$= \frac{1}{k_2} \frac{x}{a(a-x)}$$

or $$k_2 = \frac{1}{t} \frac{x}{a(a-x)} \qquad \ldots(3\cdot40)$$

This is called the integrated equation for a second-order reaction.

(*ii*) *When the initial concentrations of A and B are unequal.*

In this case, suppose the initial concentration of A is a moles lit^{-1} and that of B is b moles lit^{-1} and at any time t, x moles lit^{-1} of each have been reacted. Then, the differential rate equation will be

$$\frac{dx}{dt} = k_2(a-x)(b-x) \qquad \ldots(3\cdot41)$$

On rearranging,

$$\frac{dx}{(a-x)(b-x)} = k_2 dt \qquad \ldots(3\cdot42)$$

By partial fractions,

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] \qquad \ldots(3\cdot43)$$

Substituting in Eq. (3·42), we get

$$\frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]dx = k_2 dt \qquad \ldots(3\cdot44)$$

Integrating the right hand side of Eq. (3·44) between the limits $t=0$ and $t=t$ and the left hand side between the corresponding limits $x=0$ and $x=x$, we get

$$\frac{1}{(a-b)} \int_{x=0}^{x=x}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]dx = k_2 \int_{t=0}^{t=t} dt$$

or $$\frac{1}{a-b}\left[-\ln(b-x)+\ln(a-x)\right]_{x=0}^{x=x} = k_2\left[t\right]_{t=0}^{t=t}$$

or $$\frac{1}{a-b}\left[-\ln(b-x)+\ln(a-x)+\ln b-\ln a\right]=k_2 t$$

or $$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = k_2 t$$

or $$\frac{2{\cdot}303}{(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}=k_2t$$

or $$t=\frac{2{\cdot}303}{k_2(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)} \qquad ...(3{\cdot}45)$$

or $$k_2=\frac{2{\cdot}303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)} \qquad ...(3{\cdot}46)$$

Interval formula. If x_1 and x_2 are the concentrations of the reactant converted into products upto time t_1 and t_2 respectively, then from Eq. (3·39), we can write

$$t_1=\frac{1}{k_2(a-x_1)}-\frac{1}{k_2a} \qquad ...(3{\cdot}47)$$

and $$t_2=\frac{1}{k_2(a-x_2)}-\frac{1}{k_2a} \qquad ...(3{\cdot}48)$$

Subtracting Eq. (3·47) from Eq. (3·48), we get

$$t_2-t_1=\frac{1}{k_2}\left[\frac{1}{(a-x_2)}-\frac{1}{(a-x_1)}\right]$$

or $$t_2-t_1=\frac{1}{k_2}\frac{x_2-x_1}{(a-x_2)(a-x_1)} \qquad ...(3{\cdot}49)$$

Graphical Representation of Second-order Reaction

From Equation (3·39), *i.e.*,

$$t=\frac{1}{k_2(a-x)}-\frac{1}{k_2a}$$

it is clear that a plot between $\frac{1}{a-x}$ versus t will be a straight line with positive slope as shown in Fig. 3 6 (a).

From Eq. (3·45), *i.e.*,

$$t=\frac{2{\cdot}303}{k_2(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$$

it is evident that a plot between $\frac{1}{a-b}\log_{10}\frac{b(a-x)}{a(b-x)}$ versus t will be a straight line passing through the origin as shown in Fig. 3·6 (b).

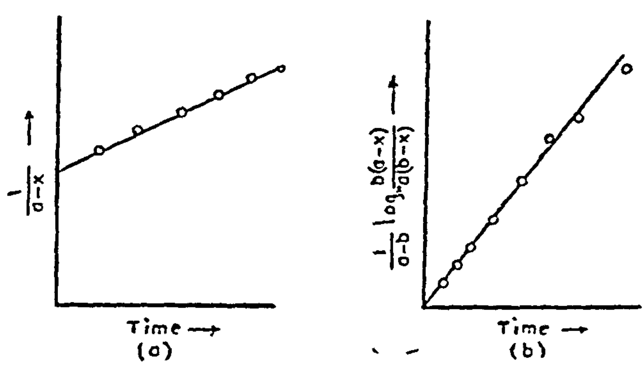


Fig. 3·6. Graphical Representation of a Second-order Reaction.

Half-life Period of Second-order Reactions

If $t = t_{1/2}$, then $x = a/2$. Putting these values in Eq. (3·40), we get

$$t_{\frac{1}{2}} = \frac{1}{k_2 a}\,\frac{a/2}{a-a/2}$$

or $$t_{\frac{1}{2}} = \frac{1}{k_2 a} \qquad \ldots(3{\cdot}51)$$

This equation shows that the **half-life period of a second-order reaction** *is inversely proportional to the first power of the initial concentration of the reactant.*

Units of k_2. The dimensions of k_2 can be obtained by putting $a+b+c+\ldots\ldots\ldots = 2$ in Eq. (3·14),

$$k_2 = \text{Conc}^{-1}\ \text{Time}^{-1} \qquad \ldots(3{\cdot}52)$$

If the concentration is expressed in terms of moles/litre and time in seconds, then the units of k_2 will be

$$k_2 = \left[\frac{\text{moles}}{\text{litre}}\right]^{-1}\text{sec}^{-1} = \text{lit mole}^{-1}\ \text{sec}^{-1}.$$

The change in the concentration units will change the numerical value of the constant.

Summary of the Characteristics of Second-order Reactions

(*i*) Differential rate equation :

$$\frac{dx}{dt} = k_2(a-x)^2 \text{ or } k_2\,(a-x)\,(b-x).$$

(*ii*) Integrated rate equations :

$$k_2 = \frac{1}{t}\cdot\frac{x}{a(a-x)}$$

$$k_2 = \frac{2{\cdot}303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$$

$$t_2 - t_1 = \frac{1}{k_2}\,\frac{x_2-x_1}{(a-x_2)(a-x_1)}.$$

(*iii*) Graphical representation. The plots—(1) $\frac{1}{a-x}$ versus t, and (2) $\frac{1}{a-b}\log_{10}\frac{b(a-x)}{a(b-x)}$ versus t are straight lines.

(*iv*) The half-life period, $t_{\frac{1}{2}} \propto \frac{1}{a}$.

(*v*) k_2 has dimensions of Conc^{-1} Time^{-1} and the change in concentration units will change the numerical value of k_2.

Example 9. *In a second-order reaction, the initial concentration of the reactant is 0·1 mole lit^{-1}. The reaction is found to be 20% complete in 40 min. Calculate (i) the rate constant, (ii) half-life period, and (iii) time required to complete 75% of the reaction.*

Solution. We know that for a second-order reaction

$$k_2 = \frac{1}{t} \frac{x}{a(a-x)}$$

Here $a = 0{\cdot}1$ mole lit^{-1}

$$x = 20\% = \frac{20}{100} \times 0{\cdot}1 = 0{\cdot}02 \text{ mole lit}^{-1}$$

$$t = 40 \text{ min}$$

$$\therefore \quad k_2 = \frac{1}{40} \cdot \frac{0{\cdot}02}{0{\cdot}1 \times (0{\cdot}1 - 0.02)}$$

$$= 0{\cdot}0625 \text{ lit mole}^{-1} \text{ min}^{-1}.$$

(*ii*) We know that the half-life period of a second-order reaction is

$$t_{\frac{1}{2}} = \frac{1}{k_2 a}$$

Here $a = 0{\cdot}1$ mole lit^{-1}

$$k_2 = 0{\cdot}0625 \text{ lit mole}^{-1} \text{ min}^{-1}$$

$$\therefore \quad t_{\frac{1}{2}} = \frac{1}{0{\cdot}1 \times 0{\cdot}0625} = 160 \text{ min}.$$

(*iii*) For calculating the time required for the completion of 75% of the reaction we can use the formula

$$t = \frac{1}{k_2 a} \frac{x}{(a-x)}$$

Here $a = 0{\cdot}1$ mole lit^{-1}

$$x = 75\% = \frac{75}{100} \; a = \frac{75}{100} \times 0{\cdot}1$$

$$= 0{\cdot}075 \text{ mole lit}^{-1}$$

and $k_2 = 0{\cdot}0625$ lit mole^{-1} min^{-1}.

$$\therefore \quad t = \frac{1}{0{\cdot}0625 \times 0{\cdot}1} \times \frac{0{\cdot}075}{(0{\cdot}1 - 0{\cdot}075)}$$

$$= \frac{0{\cdot}075}{0{\cdot}0625 \times 0{\cdot}1 \times 0{\cdot}025}$$

$$= 480 \text{ min}.$$

Examples of second-order Reactions

(*a*) **Gaseous Reactions** Second-order gaseous reactions are very common. For example, thermal dissociation of ozone, hydrogen iodide, nitrous oxide, nitrogen dioxide, acetaldehyde, chlorine monoxide and dimerization of butadiene are second order gaseous reactions. The progress of such reactions can be followed by measuring the pressure of the system, at constant volume, with the help of manometer attached to the closed reaction vessel from time to time. Let us take the following example as an illustration.

Thermal dissociation of Acetaldehyde. This is a second-order gaseous reaction and occurs according to the equation.

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO$$

The progress of the reaction can be followed by measuring the pressure of the system at different time intervals. Let P_o be the initial pressure of acetaldehyde and P be the total pressure of the system at any time t. If x is the decrease in pressure at time t, then the partial pressures of acetaldehyde, p_{CH3CHO}, methane p_{CH4} and carbon monoxide p_{CO} will be as follows :

$$p_{CH3CHO} = P_o - x \quad \text{...(i)}$$
$$p_{CH4} = p_{CO} = x \quad \text{...(ii)}$$

The total pressure of the system

$$\begin{aligned} P &= p_{CH3CHO} + p_{CH4} + p_{CO} \\ &= P_o - x + x + x \\ &= P_o + x \end{aligned}$$

or $$x = (P - P_o)$$

Substituting this value of x in Eq. (i)

$$p_{CH3CHO} = P_o - P + P_o = (2P_o - P)$$

Here P_o is proportional to the initial concentration of acetaldehyde and p_{CH3CHO} is proportional to the undissociated acetaldehyde, *i.e.*,

$$P_o \propto a$$

and $$(2P_o - P) \propto (a - x)$$

Hence $$k_2 = \frac{1}{t}\,\frac{x}{a(a-x)} = \frac{1}{t}\,\frac{(P - P_o)}{P_o(2P_o - P)}.$$

Example 10. *Hinshelwood and Hutchism studied the thermal decomposition of acetaldehyde at 518°C and obtained the following data :*

Time (sec)	*0*	*42*	*105*	*242*	*310*	*480*
Pressure (mm Hg)	*363*	*397*	*437*	*497*	*517*	*557*

Show that the reaction is of second-order and determine its rate constant.

Solution. The reaction will be of second-order if the values of rate constant obtained from the following equation shows a fair degree of constancy :

$$k = \frac{1}{t}\,\frac{(P - P_o)}{P_o(2P_o - P)}$$

Here $P_o = 363$ mm Hg

t sec	$(P - P_o)$ mm Hg	$(2P_o - P)$ mm Hg	$\frac{1}{t}\,\frac{(P-P_o)}{P_o(2P_o-P)} =$	k_2 mm Hg sec^{-1}
42	34	329	$\frac{1}{42} \times \frac{34}{363 \times 329}$	$= 6{\cdot}79 \times 10^{-6}$
105	74	289	$\frac{1}{105} \times \frac{74}{363 \times 289}$	$= 6{\cdot}71 \times 10^{-6}$

242	134	229	$\frac{1}{242}\times\frac{134}{363\times 229}=6\cdot 66\times 10^{-6}$
310	154	209	$\frac{1}{310}\times\frac{154}{363\times 209}=6\cdot 55\times 10^{-6}$
480	194	169	$\frac{1}{480}\times\frac{194}{363\times 169}=6\cdot 59\times 10^{-6}$

A fair constancy in the values of k_2 shows that the reaction is of second-order.

$$\text{The average value of } k_2 = \frac{(6\cdot 79+6\cdot 71+6\cdot 66+6\cdot 55+6\cdot 59)\times 10^{-6}}{5}$$

$$= 6\cdot 66\times 10^{-6} \text{ mm Hg sec}^{-1}.$$

Reactions in Solution

(*i*) **Saponification of an Ester by an Alkali.** The saponification of ethyl acetate by NaOH occurs according to the following equation

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

This reaction is of second-order and is conveniently studied by mixing equivalent amounts of ester and alkali solutions. The progress of the reaction can be followed by withdrawing a definite volume of reaction mixture from time to time, quenching in ice cold water and estimating the amount of unchanged alkali by titrating against a standard acid solution. Thus, the volume of acid used at the commencement of the saponification corresponds to a, and the amount of acid used at any time t corresponds to unchanged alkali, i.e., $(a-x)$. The specific reaction rate can be calculated using Eq. (3·40) If the initial concentration of ester and alkali are different then Eq. (3·46) is used.

Example 11. *In an experiment of saponification of ethyl acetate with sodium hodroxide, the progress of the reaction was measured by titrating the unchanged alkali at certain intervals. Using equal concentrations of ethyl acetate and NaOH solution, the following data were obtained :*

Time (min)	*0*	*5*	*15*	*25*	*35*	*55*
Volume of acid (ml)	*16*	*10·4*	*6·1*	*4·35*	*3·35*	*2·3*

Show that the reaction is of second-order.

Solution. The reaction will be of second-order only if the values of k_2, at different times, obtained by the following equation are constant :

$$k_2 = \frac{1}{t}\;\frac{x}{a(a-x)}.$$

The value of acid at the commencement of the reaction corresponds to a and the volume at any time t corresponds to $(a-x)$.

Here $a = 16.$

The values of k_2 at different intervals are calculated as below :

t	$a-x$	x	$\frac{1}{t}\,\frac{x}{a(a-x)}$	$=k_2$
5	10·4	5·6	$\frac{1}{5}\times\frac{5{\cdot}6}{16\times10{\cdot}4}$	$=6{\cdot}732\times10^{-3}$
15	6·1	9·9	$\frac{1}{15}\times\frac{9{\cdot}9}{16\times6{\cdot}1}$	$=6{\cdot}763\times10^{-3}$
25	4·35	11·65	$\frac{1}{25}\times\frac{11{\cdot}65}{16\times4{\cdot}35}$	$=6{\cdot}695\times10^{-3}$
35	3·35	12·65	$\frac{1}{35}\times\frac{12{\cdot}65}{16\times3{\cdot}35}$	$=6{\cdot}704\times10^{-3}$
55	2·3	13·7	$\frac{1}{55}\times\frac{13{\cdot}7}{16\times2{\cdot}3}$	$=6{\cdot}769\times10^{-3}$

A fair constancy in the value of k_2 shows that the reaction is of second-order.

2. Conversion of Ammonium Cyanate into Urea. The mechanism of the reaction is

$$(i)\quad NH_4CNO \rightleftharpoons NH_4NCO \rightleftharpoons H{-}N{=}C{=}O + NH_2 \qquad (\textit{fast})$$

$$(ii)\quad H{-}N{=}C{=}O + NH_2 \rightarrow O{=}C\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array} \qquad (\textit{slow})$$

$$NH_4CNO \rightarrow O{=}C\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array}$$

Step (*ii*) being slow is the rate determining step and hence the reaction is of second-order.

3. Benzoin condensation. In presence of alc. KCN, the condensation of two molecules of benzaldehyde into benzoin is a second-order reaction.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \longrightarrow \underset{\text{Benzoin}}{C_6H_5CH(OH)COC_6H_5}$$

4. Reaction between Persulphate and Iodide. The stoichiometric equation for the reaction is

$$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$$

The mecahanism of the reaction is

$$(i)\quad S_2O_8^{2-} \rightarrow 2SO_4^{-} \qquad (\textit{fast})$$

$$(ii)\quad SO_4^{-} + I^{-} \rightarrow I + SO_4^{2-} \qquad (\textit{slow})$$

$$(iii)\quad I + I \rightarrow I_2 \qquad (\textit{fast})$$

Step (*ii*) being slowest is the rate determining step and hence the order is two.

Third-order Reactions

A reaction is said to be of **third-order**, *if its rate depends on the cube of the concentration of one substance or to the product of the square of concentration of one substance and first power concentration of second substance, or to the product of first power concentrations of three substances.* These three types of reactions can be written as

(*i*) $3A \rightarrow$ Products

(*ii*) $2A+B \rightarrow$ Products

(*iii*) $A+B+C \rightarrow$ Products

Out of these three, (*ii*) type of reactions is most frequent.

Case I. *When a reaction involves a single substance only or more substances with equal initial concentrations.*

If a moles lit^{-1} is the initial concentration and x moles lit^{-1} of each have been reacted to give the products upto the time t, then the differential rate equation is

$$\frac{dx}{dt}=k_3(a-x)^3 \qquad ...(3\cdot53)$$

where k_3 is the rate constant for third-order reaction.

On rearranging

$$\frac{dx}{(a-x)^3}=k_3 dt \qquad ...(3\cdot54)$$

Integrating the right hand side of Eq. (3·54) between the limits $t=0$ to $t=t$ and the left hand side between the corresponding limits $x=0$ to $x=x$, we get

Suppose a and b are the initial concentrations of A and B respectively and x is the concentration change upto the time t, then the differential rate equation is given by

$$\frac{dx}{dt}=k(a-2x)^2(b-x)$$

which on integration gives

$$k_3=\frac{1}{t(a-2b)^2}\left[\frac{2x(2b-a)}{a(a-2x)}+\ln\frac{b(a-2x)}{a(b-x)}\right] \quad ...(3\cdot58)$$

(*ii*) Now consider the following reaction

A+B+C → Products

If a, b and c are the initial concentrations of A, B and C respectively and x is the concentration change upto the time t, then the differential rate equation is given by

$$\frac{dx}{dt}=k_3(a-x)(b-x)(c-x)$$

which on integration gives

$$k_3=\frac{1}{t}\left(\frac{(b-c)\ln\frac{a-x}{a}+(c-a)\ln\frac{b-x}{b}+(a-b)\ln\frac{c-x}{c}}{(b-c)(a-b)\,c-a)}\right) \quad ...(3\cdot59)$$

Graphical representation. From Eq. (3.55), it is evident that a plot between $\frac{1}{(a-x)^2}$ and t will be a straight line with positive slope.

Half-life Period. If $t=t_{\frac{1}{2}}$, then $x=a/2$. Substituting these values in Eq. (3·56), we get

$$t_{\frac{1}{2}}=\frac{1}{2k_3}\left[\frac{a/2\,(2a-a/2)}{a^2(a-a/2)^2}\right]$$

$$=\frac{3}{2k_3}\cdot\frac{1}{a^2} \quad ...(3\cdot60)$$

This equation shows that the half-life period of third-order reaction is inversely proportional to the square of the initial concentration.

Units of k_3. The dimensions of k_3 may be obtained by putting $a+b+c+...=3$ in Eq. (3·14)

$$k_3=[\text{Conc.}]^{-2}\ \text{Time}^{-1}.$$

If concentration units are moles/lit. and time is expressed in sec., then

$$k_3=\left[\frac{\text{moles}}{\text{lit}}\right]^{-2}\text{sec}^{-1}=\text{lit}^2\ \text{mole}^{-2}\ \text{sec}^{-1}.$$

Since k_3 depends on concentration terms, the change in concentration units will change the numerical value of k_3.

Summary of the Characteristics of Third-order Reactions

(i) Differential rate equations : $\frac{dx}{dt} = k_3 (a-x)^3$ or $k_3 (a-2x)^2 (b-x)$

or $k_3 (a-x)(b-x)(c-x)$

(ii) Integrated rate equations : $k_3 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$

$$k_3 = \frac{1}{t(a-2b)^2}\left[\frac{2x(2b-a)}{a(a-2x)} + \ln\frac{b(a-2x)}{a(b-x)}\right]$$

$$k_3 = \frac{1}{t}\left[\frac{(b-c)\ln\frac{a-x}{a} + (c-a)\ln\frac{b-x}{b} + (a-b)\ln\frac{c-x}{c}}{(b-c)(a-b)(c-a)}\right]$$

(iii) Graphical representation : A plot between $\frac{1}{(a-x)^2}$ and t gives a straight line

(iv) The half-life period $t_{\frac{1}{2}} \propto \frac{1}{a^2}$

(v) k_3 has dimensions of $conc^{-2}\ Time^{-1}$ and hence the change in concentration units will change the numerical value of k_3.

Examples of Third-order Reactions

(*a*) **Gaseous Reactions** Only the following five homogeneous third-order gaseous reactions are known each involving nitric oxide as one of the reactants :

$$2\,NO + O_2 \rightarrow 2\,NO_2$$
$$2\,NO + Cl_2 \rightarrow 2\,NOCl$$
$$2\,NO + Br_2 \rightarrow 2\,NOBr$$
$$2\,NO + H_2 \rightarrow N_2O + H_2O$$
$$2\,NO + D_2 \rightarrow N_2O + D_2O$$

(*b*) **Reactions in Solution.**

(*i*) **Reaction between ferric chloride and stannous chloride.** This is a very often quoted example of third order reaction in solution. This reaction is usually of second-order but under certain conditions it is of third-order. Noyes (1895) showed that the reaction takes place according to the following equations :

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

The progress of the reaction can be followed by withdrawing a definite amount of reaction mixture from time to time, adding $HgCl_2$ solution to remove excess of $SnCl_2$, and then estimating the concentration of ferrous chloride by titrating against standard potassium dichromate solution.

Example 12. *In an experiment of the reduction of $FeCl_3$ with $SnCl_2$, equivalent amounts of both the reactants were taken. The progress of the reaction was noted by withdrawing a definite amount of the reaction mixture, at different intervals of time, and run into mercuric chloride solution to destroy the excess of $SnCl_2$ and titrating with standard $K_2Cr_2O_7$ solution. The following results were obtained :*

Time (sec)	*60*	*180*	*420*	*660*	∞
Volume of $K_2Cr_2O_7$ solution (ml)	*4·78*	*8·88*	*12·04*	*13·67*	*20·83*

Show that the reaction is of third-order.

Solution. We know that for a third-order reaction, when the initial concentrations of the reactants are equal.

$$k_3 = \frac{1}{2t}\left[\frac{x\,(2a-x)}{a^2(a-x)^2}\right]$$

The volume of $K_2\,Cr_2O_7$ used at any time t corresponds to the amount of $FeCl_2$ at that time. Hence its value at infinite time, *i.e.*, at the completion of the reaction corresponds to the total amount of $FeCl_2$ formed and thus in turn is equivalent to total amount of $FeCl_3$ taken *i.e.*, a.

Thus, in this case $a = 20{\cdot}83$

The value of k_3 at different times is calculated as under :

t (sec)	x (ml)	$a-x$ (ml)	$2a-x$ (ml)	$\frac{1}{2t}\left[\frac{x(2a-x)}{a^3(a-x^2)}\right]$	$= k_3$ (lit² mole⁻² sec⁻¹)
60	4·78	16·05	36·78	$\frac{1}{2\times60}\times\frac{4{\cdot}78\times36{\cdot}88}{(20{\cdot}83)^2\times(16{\cdot}05)^2}$	$= 1{\cdot}314\times10^{-5}$
180	8·88	11·95	32·38	$\frac{1}{2\times180}\times\frac{8{\cdot}88\times32{\cdot}78}{(20{\cdot}83)^2\times(11{\cdot}95)^2}$	$= 1{\cdot}302\times10^{-5}$
420	12·04	8 79	29·62	$\frac{1}{2\times420}\times\frac{12{\cdot}04\times29{\cdot}62}{(20{\cdot}83)^2\times(8{\cdot}79)^2}$	$= 1{\cdot}296\times10^{-5}$
660	13·67	7·16	27·99	$\frac{1}{2\times660}\times\frac{13{\cdot}67\times27{\cdot}99}{(20{\cdot}83)^2\times(7{\cdot}16)^2}$	$= 1{\cdot}303\times10^{-5}$

A fair constancy in the value of k_3 shows that the reaction is of third-order.

2. A reaction between mercuric chloride and potassium oxalate is also of third order.

$$2Hg\,Cl_2 + K_2C_2O_4 \longrightarrow Hg_2\,Cl_2 + 2KCl + 2CO_2$$

3. Noyes and Cottle showed that action of sodium formate on silver acetate is of third-order.

$$2\,CH_3\,COO\,Ag + HCOONa \longrightarrow 2\,Ag + CO_2 + CH_3\,COOH + CH_3\,COONa$$

Reactions of Higher-order

Let us consider the general case of nth order reaction. The reaction may be represented as

$$nA \longrightarrow \text{Products}$$

If a is the initial concentration of A and x is the concentration decomposed upto time t, then the differential rate equation is

$$\frac{dx}{dt} = k_n\,(a-x)^n \qquad ...(3{\cdot}61)$$

where k_n is the rate constant of n th order reaction.

On rearranging Eq. (3·61), we get

$$\frac{dx}{(a-x)^n} = k_n\,dt \qquad ...(3{\cdot}62)$$

Integrating the right hand side of Eq. (3·62) between the limits $t=0$ to $t=t$ and the left hand side between the corresponding limits $x=0$ to $x=x$, we get

$$\int_{x=0}^{x=x} \frac{dx}{(a-x)^n} = \int_{t=0}^{t=t} k_n dt$$

or $$\left[\frac{1}{(n-1)\,(a-x)^{n-1}}\right]_{x=0}^{x=x} = \left[\; k_n t \;\right]_{t=0}^{t=t}$$

or $$\frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] = k_n t$$

or $$t = \frac{1}{k_n(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \qquad ...(3·63)$$

or $$k_n = \frac{1}{t\,(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \qquad ...(3·64)$$

Half-life Period. If $t=t_{\frac{1}{2}}$, then $x=a/2$. Substituting these values in Eq. (3·63), we get

$$t_{\frac{1}{2}} = \frac{1}{k_n\,(n-1)}\left[\frac{1}{(a-a/2)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$= \frac{1}{k_n\,(n-1)}\left[\frac{2^{n-1}}{a^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$= \frac{1}{k_n\,(n-1)}\,(2^{n-1}-1) \cdot \frac{1}{a^{n-1}} \qquad ...(3·65)$$

or $$t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}} \qquad ...(3·66)$$

Thus, the half-life period of n th order reaction is inversely proportinal to $(n-1)$ th power of the initial concentration.

Reactions of higher order are very rare. This has already been explained on the basis of molecular collision theory in the mechanism of chemical reactions. However, the following reactions have been reported to be of fourth order :

(*i*) **Thermal decomposition of $KClO_3$**

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl$$

(*ii*) **The reaction between HBr and BrO_3^-**

$$2H^+ + Br^- + BrO_3^- \longrightarrow HBrO + HBrO_2$$

Zero-order Reactions.

According to the definition of order of reaction, *a reaction is said to be of* **Zero order** *if its rate is proportional to the zeroth power of the initial concentration of the reactant, i.e.,*

$$\frac{dx}{dt} = kc^{\circ} = k$$

Thus, we see that in a zero-order reaction, the rate of reaction is independent of the reaction concentration and remains constant throughout the course of reaction.

For example, photochemical combination of H_2 and Cl_2 over water at constant pressure is of zero-order reaction. This can be easily seen if the mixture of equal volumes of H_2 and Cl_2 gases is filled in a long tube closed at one end. The other end is dipped in water. The tube is then exposed to sunlight. The reaction starts and the course of the reaction can be followed by noting the rate of the water level because the amount of HCl formed gets absorbed by water instantaneously and the level of water rises to maintain the constancy of pressure. Here, we see that the amounts of H_2 and Cl_2 are decreasing but their concentration, *i.e.*, amount per unit volume remains constant in the reaction space because the reaction space is also decreasing with the increase of water level. Hence, the reaction is of zero-order.

Degeneration of the Reaction-order.

If the rate equation for a general reaction is given by

$$\frac{dx}{dt} = kc_A^a\ c_B^b\ c_C^c\cdots\cdots$$

then the reaction order $n = a+b+c+\ldots\ldots$But, if the conditions of the reaction are altered in such a way that the concentration of one or more of the reactants remain constant throughout the reaction course, the reaction order will be degenerated. This may happen in two ways :

(*i*) **When one of the reactants is present in large excess over the others**. For example, take a general second order reaction

$$A + B \longrightarrow \text{Products.}$$

In this case the order of reaction with respect to A is one and with respect to B is one and hence the total order is two. Now, if B is present in large excess with respect to A, then the change in the concentration of B will be negligible and hence the rate will become independent of the concentration of B. Thus, the order of reaction with respect to B will be zero and the total order will now be one. This shows the degeneration of the order. This can also be shown mathematically using the following integrated rate equation for this reaction :

$$k_2 = \frac{2\cdot303}{t\,(a-b)} \log_{10} \frac{b\,(a-x)}{a\,(b-x)}$$

If b $>>$ a, then $b-x \cong b$ and $a-b \cong -$b. Substituting these values in the above equation, we get

$$k_2 = -\frac{2\cdot303}{t\,b} \log_{10} \frac{b\,(a-x)}{ab}$$

$$= \frac{2\cdot303}{t\,b} \log_{10} \frac{a}{a-x}$$

$$\text{or} \quad k_2 b = \frac{2 \cdot 303}{t} \log_{10} \frac{a}{a-x}$$

Since b is in large excess, it can be taken as constant. Hence writing $k_2 b = k_1$, we obtain

$$k_1 = \frac{2 \cdot 303}{t} \log_{10} \frac{a}{a-x}$$

This is a typical equation of first-order reaction. The new constant k_1, of course, depends on the initial concentration of B.

(*ii*) **When one of the reactant is not in excess but its concentration is maintained constant.** This situation arises when one of the reactant is catalyst (the concentration of which does not alter after the completion of the reaction) or it is regenerated as soon as it is consumed. Thus, the order with respect to this reactant will become zero and the overall order will be degenerated. However, the rate will depend on its initial concentration.

Determination of the Order of a Reaction

There are various methods of determining the order of a reaction. *Some commonly used methods are described below :*

(*i*) Use of Integrated Rate equations

The progress of the reaction is followed by measuring concentrations of either a reactant or a product from time to time. These values are then substituted in the integrated rate equations for the first, second, and third-order reactions. The equation which gives reasonably constant value of k determines the order of reaction. It is also known as **hit and trial** method because it involves the trial of one equation after another till the best suited equation is found out. The disadvantage of this method is that it is applicable to simpler reactions only and further a number of readings over a wide time intervals are to be taken for getting satisfactory results.

(*ii*) Fractional-change Method

As already discussed that for a reaction of nth order, the time t_1 required to complete a definite fraction of the reaction is inversely proportional to $(n-1)$th power of the initial concentration a of the reactant, *i.e.*,

$$t \propto \frac{1}{a^{n-1}}$$

Let us consider that two experiments are carried out with different initial concentrations a_1 and a_2. If t_1 and t_2 are the times required to complete the same fraction of change, then

$$t_1 \propto \frac{1}{a_1^{n-1}} \qquad \ldots(3 \cdot 67)$$

$$\text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Thus, we see that in a zero-order reaction, the rate of reaction is independent of the reaction concentration and remains constant throughout the course of reaction.

For example, photochemical combination of H_2 and Cl_2 over water at constant pressure is of zero-order reaction. This can be easily seen if the mixture of equal volumes of H_2 and Cl_2 gases is filled in a long tube closed at one end. The other end is dipped in water. The tube is then exposed to sunlight. The reaction starts and the course of the reaction can be followed by noting the rate of the water level because the amount of HCl formed gets absorbed by water instantaneously and the level of water rises to maintain the constancy of pressure. Here, we see that the amounts of H_2 and Cl_2 are decreasing but their concentration, *i.e.*, amount per unit volume remains constant in the reaction space because the reaction space is also decreasing with the increase of water level. Hence, the reaction is of zero-order.

Degeneration of the Reaction-order.

If the rate equation for a general reaction is given by

$$\frac{dx}{dt} = kc_A^a \; c_B^b \; c_C^c \ldots\ldots$$

then the reaction order $n = a+b+c+\ldots\ldots$ But, if the conditions of the reaction are altered in such a way that the concentration of one or more of the reactants remain constant throughout the reaction course, the reaction order will be degenerated. This may happen in two ways :

(*i*) **When one of the reactants is present in large excess over the others.** For example, take a general second order reaction

$$A + B \longrightarrow \text{Products.}$$

In this case the order of reaction with respect to A is one and with respect to B is one and hence the total order is two. Now, if B is present in large excess with respect to A, then the change in the concentration of B will be negligible and hence *the rate will become independent of the concentration of* B. Thus, the order of reaction with respect to B will be zero and the total order will now be one. This shows the degeneration of the order. This can also be shown mathematically using the following integrated rate equation for this reaction :

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If b $>>$ a, then $b-x \cong b$ and $a-b \cong -b$. Substituting these values in the above equation, we get

$$k_2 = -\frac{2 \cdot 303}{t\,b} \log_{10} \frac{b\,(a-x)}{ab}$$

$$= \frac{2 \cdot 303}{t\,b} \log_{10} \frac{a}{a-x}$$

$$= 1 + \frac{0.1734}{0.1761} = 1.9842$$

$$\simeq 2$$

Hence, the order of the reaction is 2.

Example 14. *Hinshelwood studied the thermal decomposition of phosphine, and obtained the following data :*

Initial (mm Hg)	*707*	*79*	*37·5*
Half-life (min)	*1·4*	*1·4*	*1·4*

Find the order of the reaction.

Solution Since half-life period is constant for all the various pressures, it is independent of initial pressure. It is, therefore, a first order reaction.

3. Graphical Method.

The order of reaction may be determined by plotting different appropriate functions of $(a-x)$ *i.e.*, amount of unreacted reactant versus t.

If a straight line is obtained on plotting $\log_{10}(a-x)$ or $\log_{10} \dfrac{a}{a-x}$ versus t, the reaction is of first-order.

If a straight line is obtained on plotting $\dfrac{1}{a-x}$ versus t, the reaction is of second-order.

Similarly, if a straight line is obtained by plotting $\dfrac{1}{(a-x)^2}$ versus t, the reaction is of third-order.

There is another way of determining the order of a reaction graphically. Let us consider a general reaction of nth order with the same initial concentration of the reactants. The differential rate equation for such reaction is given by :

$$\frac{dx}{dt} = k_n(a-x)^n$$

Taking logarithm of both the sides, we get

$$\log_{10}\left(\frac{dx}{dt}\right) = \log_{10} k_n (a-x)^n$$

or $$\log_{10}\left(\frac{dx}{dt}\right) = n \log_{10}(a-x) + \log_{10} k_n$$

If $\log_{10}(dx/dt)$ is plotted against $\log_{10}(a-x)$, a straight line is obtained and the slope determines the value of n.

The values of $(a-x)$ or x, depending upon the experimental convenience, are plotted against t. The values of $-\dfrac{d(a-x)}{dt}$ or $\dfrac{dx}{dt}$ at

Dividing Eq. (3·68) by Eq. (3·67), we get

$$\frac{t_2}{t_1}=\left[\frac{a_1}{a_2}\right]^{n-1} \qquad ...(3\cdot69)$$

Taking logarithm of both the sides, we get

$$\log_{10}\frac{t_2}{t_1}=\log_{10}\left[\frac{a_1}{a_2}\right]^{n-1}$$
$$=(n-1)\log_{10}(a_1/a_2)$$

or $$n-1=\frac{\log_{10}(t_2/t_1)}{\log_{10}(a_1/a_2)}$$

or $$n=1+\frac{\log_{10}(t_2/t_1)}{\log_{10}(a_1/a_2)}$$

or $$n=1+\frac{\log_{10}t_2-\log_{10}t_1}{\log_{10}a_1-\log_{10}a_2} \qquad ...(3\cdot70)$$

Thus, the order can be calculated.

Example 13. *The following results refer to the decomposition of acetaldehyde at 518°C*

Initial pressure (mm Hg)	*70*	*120*	*180*
Half-life (sec)	*1400*	*820*	*550*

Determine the order of the reaction.

Solution. We know that

$$n=1+\frac{\log_{10}t_2-\log_{10}t_1}{\log_{10}a_1-\log_{10}a_2}$$

Since it is gaseous reaction, the concentration terms a_1 and a_2 can be replaced by the pressure terms P_1 and P_2. Thus,

$$n=1+\frac{\text{og}_{10}t_2-\log_{10}t_1}{\log_{10}P_1-\log_{10}P_2}$$

(*i*) **For first pair**

$p_1 = 70$ mm Hg $t_1 = 1400$ sec
$p_2 = 120$ mm Hg $t_2 = 820$ sec

$$\therefore n=1+\frac{\log_{10}820-\log_{10}1400}{\log_{10}70-\log_{10}120}$$
$$=1+\frac{0\cdot2323}{0\cdot2341}=1\cdot9924$$
$$\simeq 2$$

(*ii*) **For second pair**

$p_1 = 120$ mm Hg $t_1 = 820$ sec.
$p_2 = 180$ mm Hg $t_2 = 550$ sec.

$$\therefore n=1+\frac{\log_{10}550-\log_{10}820}{\log_{10}120-\log_{10}180}$$

The differential rate equation is given by

$$\frac{dx}{dt} = k\, c_A^{a}\, c_B^{b}\, c_C^{c} \ldots$$

First all the reactants except A are taken in large excess and the order of the reaction a, is determined by any of the methods described above. Thus, a will be the order of reaction with respect to A.

Again in the second experiment, all the reactants except B are taken in large excess and the order, b, is determined. Thus, b will be the order of the reaction with respect to B.

In the same way the experiment is repeated by taking all the reactants in large excess except one and the order with respect to each of the reactant taken in small amount is determined. The overall order of the reaction will be the sum of the orders with respect to each reactant. Thus,

$$n = a + b + c + \ldots\ldots$$

6 By Varying the Ratio of Reactant by a Definite factor.

Consider the following reaction involving two reactants ;

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow \text{Products}$$

The differential rate equation is given by

$$\frac{dx}{dt} = k c_A^{a}\, c_B^{b}$$

For a short interval of time Δt, dx/dt may be replaced by $\Delta x/\Delta t$. Starting with certain concentrations of A and B, the value of $\Delta x/\Delta t$ is determined. Then the concentration of B is kept fixed and that of A is doubled and again $\Delta x/\Delta t$ is determined for the same interval of time.

In the first case

$$\left(\frac{\Delta x}{\Delta t}\right)_{\mathrm{I}} = k c_A^{a}\, c_B^{b} \tag{3·75}$$

and in the second case

$$\left(\frac{\Delta x}{\Delta t}\right)_{\mathrm{II}} = k\,(2c_A)^{a}\, c_B^{b} \tag{3·76}$$

Dividing Eq. (3·76), by Eq. (3·75), we get

$$\left(\frac{\Delta x}{\Delta t}\right)_{\mathrm{II}} \Big/ \left(\frac{\Delta x}{\Delta t}\right)_{\mathrm{I}} = \frac{k\,(2c_A)^{a}\, c_B^{b}}{k\, c_A^{a}\, c_B^{b}} = 2^{a} \tag{3·77}$$

Thus, the value of a can be determined which is the order of the reaction with respect to A.

In the same way by doubling the concentration of B and keeping the concentration of A constant, the order of reaction with res-

different times corresponding to various values of $(a-x)$ are obtained from the slopes of the curve at particular points. Then, logarithm of various values of $\frac{dx}{dt}$ are plotted against the logarithm of their corresponding values of $(a-x)$. This gives a straight line, the slope of which is equal to the order of reaction. A schematic representation of this method is shown in Fig. 3·7.

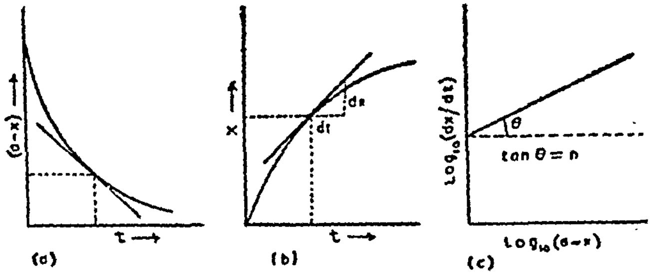


Fig. 3·7. (*a*) and (*b*) Determination of dx/dt. (*c*) Determination of the Order of Reaction *n*.

4. van't Hoff Differential Method

The differential rate equation of the *n*th order reaction is given by

$$-\frac{dc}{dt} = k_n c^n \qquad \text{...(3·71)}$$

where *c* is the concentration of the reactant at any time *t*.

Taking logarithm of both the sides of Eq. (3·71), we get

$$\log_{10}(-dc/dt) = n \log_{10} c + \log_{10} k_n$$

For two different times t_1 and t_2, let the concentrations of the reactant be c_1 and c_2 respectively. Then, we can write

$$\log_{10}(-dc_1/dt) = n \log_{10} c_1 + \log_{10} k_n \qquad \text{...(3·72)}$$

$$\log_{10}(-dc_2/dt) = n \log_{10} c_2 + \log_{10} k_n \qquad \text{...(3·73)}$$

Subtracting Eq. (3·72) from Eq. (3·73), we get

$$\log_{10}(-dc_2/dt) - \log_{10}(-dc_1/dt) = n \log_{10} c_2 - n \log_{10} c_1$$
$$= n(\log_{10} c_2 - \log_{10} c_1)$$

or $$n = \frac{\log_{10}(-dc_2/dt) - \log_{10}(-dc_1/dt)}{\log_{10} c_2 - \log_{10} c_1} \qquad \text{....(3·74)}$$

The values of $(-dc_1/dt)$ and $(-dc_2/dt)$ can be obtained from the experimental curve of *c* versus *t* by taking the slopes of the curve at c_1 and c_2.

5. Ostwald's Isolation Method

This method is applicable to those reactions which involve two or more reacting substances. Consider the following general reaction:

$$aA + bB + cC + \ldots\ldots \longrightarrow \text{Products.}$$

The differential rate equation is given by

$$\frac{dx}{dt} = k\, c_A^a\, c_B^b\, c_C^c \ldots$$

First all the reactants except A are taken in large excess and the order of the reaction a, is determined by any of the methods described above. Thus, a will be the order of reaction with respect to A.

Again in the second experiment, all the reactants except B are taken in large excess and the order, b, is determined. Thus, b will be the order of the reaction with respect to B.

In the same way the experiment is repeated by taking all the reactants in large excess except one and the order with respect to each of the reactant taken in small amount is determined. The overall order of the reaction will be the sum of the orders with respect to each reactant. Thus,

$$n = a+b+c+\ldots\ldots$$

6 By Varying the Ratio of Reactant by a Definite factor.

Consider the following reaction involving two reactants :

$$a\,A+b\,B \rightarrow \text{Products}$$

The differential rate equation is given by

$$\frac{dx}{dt} = k c_A^a\, c_B^b$$

For a short interval of time Δt, dx/dt may be replaced by $\Delta x/\Delta t$. Starting with certain concentrations of A and B, the value of $\Delta x/\Delta t$ is determined. Then the concentration of B is kept fixed and that of A is doubled and again $\Delta x/\Delta t$ is determined for the same interval of time.

In the first case

$$\left(\frac{\Delta x}{\Delta t}\right)_{I} = k c_A^a\, c_B^b \tag{3·75}$$

and in the second case

$$\left(\frac{\Delta x}{\Delta t}\right)_{II} = k\,(2c_A)^a\, c_B^b \tag{3·76}$$

Dividing Eq. (3·76), by Eq. (3·75), we get

$$\left(\frac{\Delta x}{\Delta t}\right)_{II} \bigg/ \left(\frac{\Delta x}{\Delta t}\right)_{I} = \frac{k\,(2c_A)^a\, c_B^b}{k\, c_A^a\, c_B^b} = 2^a \tag{3·77}$$

Thus, the value of a can be determined which is the order of the reaction with respect to A.

In the same way by doubling the concentration of B and keeping the concentration of A constant, the order of reaction with res-

pect to B, *i.e.*, b can be obtained. Thus, $(a+b)$ gives the overall order of the reaction.

Example 15. *The equation for the reaction between potassium oxalate and mercuric chloride is*

$$2HgCl_2+K_2C_2O_4 \rightarrow 2KCl+2CO_2+Hg_2Cl_2$$

The progress of the reaction was followed by weighing the precipitate of Hg_2Cl_2 formed at different intervals of time. The experiment was repeated using different proportions of the reactants and the following data were obtained :

	$HgCl_2$ (moles/litre)	$K_2C_2O_4$ (moles/litre)	Time (min.)	Precipitated Hg_2Cl_2 (moles)
I	0·1672	0·808	65	0·0136
II	0·1672	0·404	120	0·0062
III	0·0836	~~0·808~~ 0·404	60	0·0063

Find out the order of reaction.

Solution. The differential rate equation for this reaction may be written as

$$\frac{dx}{dt} = k \ c^a{}_{HgCl_2} \cdot c^b{}_{K_2C_2O_4}$$

From the I, II and III experiments,

$$\text{(i)} \quad \left(\frac{\Delta x}{\Delta t}\right)_{\text{I}} = \frac{0{\cdot}0136}{65} = k \ (0{\cdot}1672)^a \ (0{\cdot}808)^b$$

$$\text{(ii)} \quad \left(\frac{\Delta x}{\Delta t}\right)_{\text{II}} = \frac{0{\cdot}0062}{120} = k \ (0{\cdot}1672)^a \ (0{\cdot}404)^b$$

$$\text{(iii)} \quad \left(\frac{\Delta x}{\Delta t}\right)_{\text{III}} = \frac{0{\cdot}0063}{60} = k \ (0{\cdot}836)^a \ \cancel{(0{\cdot}808)^b} \ (0{\cdot}404)^b$$

Dividing Eq. (*i*) by Eq. (*ii*), we get

$$\left(\frac{\Delta x}{\Delta t}\right)_{\text{I}} \bigg/ \left(\frac{\Delta x}{\Delta t}\right)_{\text{II}} = \frac{0{\cdot}0136/65}{0{\cdot}0062/120} = \frac{k\,(0{\cdot}1672)^a \ (0{\cdot}808)^b}{k\,(0{\cdot}1672)^a \ (0{\cdot}404)^b} = 2^b$$

or $\qquad 2^b = 4$ (approx)

or $\qquad b = 2$

Thus, the order of reaction with respect to B is 2. Again, by dividing Eq. (*ii*) by Eq. (*iii*), we get

$$\left(\frac{\Delta x}{\Delta t}\right)_{\text{II}} \bigg/ \left(\frac{\Delta x}{\Delta t}\right)_{\text{III}} = \frac{0{\cdot}0062/120}{0{\cdot}0063/60} = \frac{k\,(0{\cdot}1672)^a \ (0{\cdot}404)^b}{k\,(0{\cdot}863)^a \ (0{\cdot}404)^b} = 2^a$$

or $\qquad 2^a = 2$ (approx)

Thus, the order of reaction with respect to A is 1.

$\therefore$ The overall order of reaction $= 2+1 = 3$.

Order and Mechanism of Reactions

Now we shall see how does the reaction order help to know the mechanism of chemical reaction. It has already been mentioned that the molecularity and the order are generally same in an elemen-

tary process. Thus reaction order gives a direct indication to the number of molecules involved in the rate determining step.

To know the mechanism of chemical reaction, first a rate equation for the reaction is established by studying the effect of concentrations of the reactants on the reaction rate. The rate equation gives indication of the complexity of rate determining step. Using this equation and the knowledge of general chemistry, a mechanism of the reaction is imagined. The postulated mechanism must show that the experimental rate constant is either equal to the rate constant for the rate determining step or equal to some algebraic combination of rate constants and equilibrium constants. With these points in mind, we shall discuss reaction mechanisms of various order reactions.

First-order reactions. If the order of reaction is one, it implies that only one molecule is undergoing chemical change in the rate determining step. For example, the stoichiometric equation for the decomposition of azomethane is given by

$$CH_3N{=}NCH_3 \rightarrow C_2H_6+N_2$$

This is first-order reaction. The experimental rate equation of this reaction is found to be

$$\text{rate} = k\,[CH_3N{=}NCH_3]$$

From the equation it is evident that only one molecule is taking part in the rate determining step. This shows that the reaction is elementary one and taking place in one step only as shown by the stoichiometric equation given above.

Take another example of the decomposition of N_2O_5. The stoichiometric equation is given by

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

The experimental rate equation is found to be

$$\text{rate} = k\,[N_2O_5]$$

which shows that the reaction is of first-order. The mechanism of the reaction should be such that it must involve a step in which only one molecule of N_2O_5 decomposes and this should be the rate determining step. This suggests a multi-step reaction. The probable mechanism is

$$\begin{array}{rcll} N_2O_5 & \rightarrow & N_2O_3+O_2 & \textit{slow} \\ N_2O_3 & \rightarrow & NO+NO_2 & \textit{fast} \\ NO+N_2O_5 & \rightarrow & 3NO_2 & \textit{fast} \end{array}$$

The slowest step conforms to the rate equation,

Second-order reactions. If the reaction order is two, it implies that two molecules are involved in the rate determining step. For example, the reaction between H_2 and I_2 is given by

$$H_2+I_2 \rightarrow 2HI$$

The experimental rate equation is found to be

$$\text{rate} = k\,[H_2]\,[I_2]$$

The rate equation indicates clearly that the rate determining step involves the collision of one molecule of H_2 and one molecule of I_2. Thus, the reaction is elementary one and takes place in one step only.

The order of the following reaction

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

is two. The experimental rate equation is found to be

$$\text{rate} = k\,[NO_2]\,[F_2]$$

The rate equation shows that the rate determining step involves one molecule of NO_2 and one molecule of F_2. The postulated mechanism for the reaction is

$$NO_2 + F_2 \longrightarrow NO_2F + F \qquad \textit{slow}$$
$$F + NO_2 \longrightarrow NO_2F \qquad \textit{fast}$$

The slow step conforms to the rate equation.

Third-order reactions. If the reaction order is three then three molecules should involve in the rate determining step. The simultaneous collisions of three molecules are not very probable, hence in most of the third-order reactions the rate determining step involves two molecules and is preceeded by a step involving equilibrium. The following example will make this point clear.

The overall reaction of the reduction of NO by H_2 is given by

$$2NO + 2H_2 \longrightarrow 2H_2O + N_2$$

The experimental rate equation is found to be

$$\text{rate} = k\,[NO]^2\,[H_2]$$

The reaction is of third order—second order with respect to NO and first order with respect to H_2. Two mechanisms of this reaction are possible and both conform to the rate equation.

(*a*)

$$2NO + H_2 \rightarrow N_2 + H_2O_2 \qquad \textit{slow}$$
$$H_2O_2 + H_2 \rightarrow 2H_2O \qquad \textit{fast}$$

The slow step conforms to the rate equation.

(*b*)

$$2NO \rightleftharpoons N_2O_2 \qquad \textit{fast at equilibrium}$$
$$N_2O_2 + H_2 \rightarrow N_2 + H_2O_2 \qquad \textit{slow}$$
$$H_2O_2 + H_2 \rightarrow 2H_2O \qquad \textit{fast}$$

According to this mechanism the rate equation will be

$$\text{rate} = k\,[N_2O_2]\,[H_2]$$

The first step involves an equilibrium, the equilibrium constant is given by

$$K = \frac{[N_2O_2]}{[NO]^2}$$

or $$[N_2O_2] = K[NO]^2$$

$\therefore$ $$\text{rate} = kK[NO]^2[H_2]$$
$$= k'[NO]^2[H_2]$$

where $k' = kK$. This equation also conforms to the experimental rate equation.

Now the question arises as to which of the two mechanisms is correct. Experimental evidences show the presence of N_2O_2 in the reaction mixture, hence the second mechanism is correct and the first one is discarded.

Fractional-order reactions. The transformation of H_2 (*para*) into H_2(*ortho*) is given by

$$H_2(para) \rightarrow H_2(ortho)$$

The experimental rate equation is found to be

$$\text{rate} = k[H_2(para)]^{3/2}$$

Thus, the order is 3/2, which shows the complex nature of the reaction. To interpret this order the following mechanism may be imagined :

$$H_2(para) \rightleftharpoons 2H \qquad \text{...Fast at equilibrium}$$
$$H_2(para) + 2H \rightarrow 2H_2(ortho) \cancel{+H} \qquad \text{...slow}$$

According to the slow step, the rate is given by

$$\text{rate} = k[H_2(para)][H]$$

The first step involves an equilibrium, the equilibrium constant K is given by

$$K = \frac{[H]^2}{[H_2(para)]}$$

or $$[H] = K^{1/2}[H_2(para)]^{1/2}$$

$\therefore$ $$\text{rate} = kK^{1/2}[H_2(para)]^{1/2}[H_2(para)]$$
$$= k'[H_2(para)]^{3/2}$$

where $k' = kK^{1/2}$. This equation conforms to the experimental rate equation.

We have discussed the mechanisms of some simple reactions. Mechanisms of more complicated reactions are beyond the scope of this book.

Influence of Temperature on Reaction Rates

In general, the rate of a chemical reaction increases shar with the increase in temperature, no matter whether the reactior

endothermic or exothermic. The change in rate is generally expressed by the change in specific reaction rate k. It has been observed in large number of cases that for a increase in temperature by 10°C the rate of a reaction or specific reaction rate is doubled or trebled. If k_t is the rate constant at t°C and k_{t+10} is the rate constant at $(t+10)$°C, then

$$\frac{k_{t+10}}{k_t} \approx 2 \text{ to } 3 \qquad ...(3\cdot78)$$

The ratio of rate constants at temperature difference by 10°C is called **temperature coefficient.** Thus, the temperature coefficient of most of the reactions lies between 2 and 3. It is an approximate method of showing the effect of temperature on the reaction rate. It is not applicable to every case. For example, the temperature coefficient of the reaction of oxidation of potassium oxalate by bromine is 6 and by iodine is 7·2. Also in certain cases, the temperature coefficient is less than one, which shows that the rate of reaction is retarded by increasing the temperature. For example, the velocity of the reaction, $2NO+O_2 \rightarrow 2NO_2$ decreases with the rise of temperature. Also the temperature coefficient of the reaction between iodate and bisulphite in presence of iodide is 0·85. Of course, these reactions have complex mechanisms.

Now a question arises—why does the temperature rise increase the reaction rate to such a great extent ? Formerly, it was tried to give the answer on the basis that the rate of the reaction is proportional to the number of collisions between the reacting molecules per second. But calculations show that for 10°C rise in temperature, the number of collisions increases by about 2% only, whereas the rate increases by 200% to 300%. Hence this theory is quite inadequate to explain the temperature effect on the reaction rate.

Arrhenius Theory. Arrhenius (1889) showed empirically that the rate constant k is related to the absolute temperature T, by the following equation :

$$k = Ae^{-E/RT} \qquad ...(3\cdot79)$$

where A is called the **pre-exponential factor,** and E is called the **activation energy.** This equation is called the **Arrhenius equation.**

Arrhenius proposed this equation purely on experimental basis. Further, he developed a simple and quantitative theory based on the kinetic molecular model which gave a sound interpretation of the relation given above. The salient features of the theory are :

(*i*) All the molecules present cannot take part in the chemical reaction but only **active** or **elevated** molecules can react.

(*ii*) The active molecules possess some excess energy above the energy possessed by an average reactant molecule. *The minimum amount of excess energy required by the reacting molecules to react is known as the* **energy of activation** .

(*iii*) The active molecules acquire the energy of activation due to collisions among the molecules.

(*iv*) There exists an equilibrium between the normal and the active molecules.

(*v*) When active molecules collide, they first form some higher energy species, which is called **activated complex.** The activated complex then breaks into the products. The rate of reaction depends on the concentration of the activated molecules.

With these features in mind, it is very easy to deduce the Arrhenius equation. The number of activated molecules having energy E greater than the average reactant molecules at temperature T, is given by the Boltzmann distribution law.

$$\frac{\text{Number of activated molecules}}{\text{Total number of reactant molecules}} = e^{-E/RT} \qquad \text{...(3·80)}$$

Since the reaction occurs only when active molecules collide, hence

$$\text{Rate of reaction} \propto \text{No. or conc. of activated molecules}$$
$$= A(\text{No. or conc. of activated molecules}) \qquad \text{...(3·81)}$$

From Eqs. (3·80) and (3·81), we obtain

$$\text{Rate of reaction} = Ae^{-E/RT}\,(\text{No. or conc. of reactant molecules}) \qquad \text{...(3·82)}$$

Since specific reaction rate

$$k = \frac{\text{rate of reaction}}{\text{conc. of reactant molecules}}$$

Hence from Eq. (3·82), we can write

$$k = Ae^{-E/RT}$$

which is Arrhenius equation. E has the dimensions of energy and is generally expressed in kcal mole^{-1}. A has the dimensions of rate constant, *e.g.*, sec^{-1} for a first-order reaction, lit mole^{-1} sec^{-1} for the second-order reaction and so on.

Determination of the energy of Activation

The Arrhenius equation is

$$k = Ae^{-E/RT}$$

Taking logarithm of both the sides, we get

$$\ln k = \ln\left(Ae^{-E/RT}\right) = \ln A - \frac{E}{RT}$$

$$\text{or} \quad 2{\cdot}303 \log_{10} k = 2{\cdot}303 \log_{10} A - \frac{E}{RT}$$

$$\text{or} \quad \log_{10} k = -\frac{E}{2{\cdot}303\,R}\left(\frac{1}{T}\right) + \log_{10} A \qquad \ldots(3{\cdot}83)$$

This equation shows, that a plot between $\log_{10} k$ and $\frac{1}{T}$ gives a straight line with a slope equal to $-\frac{E}{2{\cdot}303\,R}$ and the intercept equal to $\log_{10} A$. Thus, the value of E can be obtained from the slope.

Example 16. *The first-order rate constant k for the decomposition of N_2O_5 at various temperatures are given below :*

T (°K)	273	298	308	318	328
k (sec^{-1})	$7{\cdot}87\times10^{-7}$	$3{\cdot}46\times10^{-5}$	$1{\cdot}35\times10^{-4}$	$4{\cdot}98\times10^{-4}$	$1{\cdot}50\times10^{-3}$

Detremine the energy of activation of the reaction.

Solution : We know that if $\log_{10} k$ is plotted against $\frac{1}{T}$, a straight line with the slope $-\frac{E}{2{\cdot}303\,R}$ is obtained.

From the above table

$\log_{10}k$	$-6{\cdot}104$	$-4{\cdot}4609$	$-3{\cdot}8697$	$-3{\cdot}3028$	$-2{\cdot}8239$
$\frac{1}{T}$	$3{\cdot}66\times10^{-3}$	$3{\cdot}36\times10^{-3}$	$3{\cdot}25\times10^{-3}$	$3{\cdot}14\times10^{-3}$	$3{\cdot}05\times10^{-3}$

The values of $\log_{10}k$ and $\frac{1}{T}\times10^3$ are plotted in Fig. 3·8.

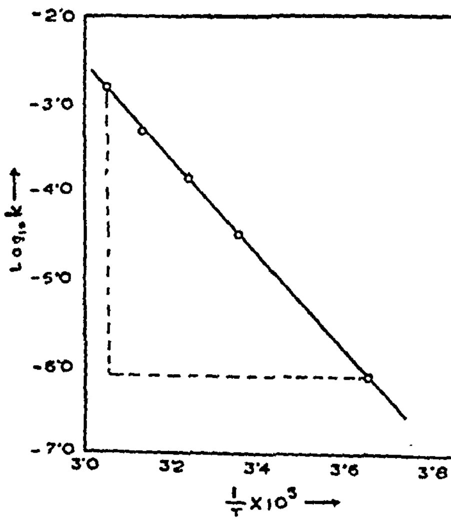


Fig. 3·8. Graph of $\log_{10}k$ versus $10^3/T$ for the Decomposition of N_2O_5

$$\text{Slope} = \frac{-6{\cdot}104-(-2{\cdot}8239)}{(3{\cdot}66-3{\cdot}05)\times10^{-3}}$$

$$= -\frac{3 \cdot 2801}{0 \cdot 61 \times 10^{-3}}$$

$$\therefore -\frac{E}{2 \cdot 303 \times R} = -\frac{3 \cdot 2801}{0 \cdot 61 \times 10^{-3}}$$

$$\text{or} \quad E = \frac{3 \cdot 2801 \times 2 \cdot 303 \times R}{0 \cdot 61 \times 10^{-3}}$$

$$= \frac{3 \cdot 2801 \times 2 \cdot 303 \times 1 \cdot 987}{0 \cdot 61 \times 10^{-3}} \text{ cal mole}^{-1}$$

$$= 24730 \text{ cal mole}^{-1}$$

The energy of activation of the decomposition of N_2O_5 is 24730 cal mole^{-1}.

There is another way of determining the energy of activation if the rate constants at two temperatures are known. Suppose k_1 and k_2 are the rate constants of a reaction at temperatures T_1 and T_2 respectively, then from Eq. (3·83), we get

$$\log_{10} k_1 = -\frac{E}{2 \cdot 303\ R}\left(\frac{1}{T_1}\right) + \log_{10} A \quad ....(3 \cdot 84)$$

$$\log_{10} k_2 = -\frac{E}{2 \cdot 303\ R}\left(\frac{1}{T_2}\right) + \log_{10} A \quad ...(3 \cdot 85)$$

Subtracting Eq. (3·84) from Eq. (3·85), we obtain

$$\log_{10} k_2 - \log_{10} k_1 = -\frac{E}{2 \cdot 303\ R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\text{or} \quad \log_{10} \frac{k_2}{k_1} = -\frac{E}{2 \cdot 383\ R}\left[\frac{T_1 - T_2}{T_1\ T_2}\right]$$

$$\text{or} \quad \log_{10} \frac{k_2}{k_1} = \frac{E}{2 \cdot 303}\left[\frac{T_2 - T_1}{T_1\ T_2}\right]$$

Example 17. *The specific reaction rates for the reaction between 2 : 4 dinitrobenzene with pyridine at 25°C and 0°C were found to be 1·11 lit mole^{-1} min^{-1} and 0·2 lit mole^{-1} min^{-1} respectively. Calculate the energy of activation of the reaction.*

Solution. We know that

$$\log_{10} \frac{k_2}{k_1} = \frac{E}{2 \cdot 303\ R}\left[\frac{T_2 - T_1}{T_1\ T_2}\right]$$

Here $k_1 = 1 \cdot 11$ lit mole^{-1} min^{-1}

$k_2 = 0 \cdot 2$ lit mole^{-1} min^{-1}

$T_1 = 273 + 25 = 298°K$

$T_2 = 273°K$

and $R = 1 \cdot 987$ cal deg^{-1} mole^{-1}

$$\therefore \log_{10} \frac{0 \cdot 2}{1 \cdot 11} = \frac{E}{2 \cdot 803 \times 1 \cdot 987}\left[\frac{273 - 298}{298 \times 273}\right]$$

$$\text{or} \quad -0 \cdot 7743 = -\frac{E}{2 \cdot 308 \times 1 \cdot 987}\left(\frac{25}{298 \times 278}\right)$$

$$\text{or} \quad E = \frac{0 \cdot 7743 \times 2 \cdot 303 \times 1 \cdot 987 \times 298 \times 2}{25}$$

$$= 11090 \text{ cal mole}^{-1}$$

It is interesting to note that the marked influence of temperature on the reaction rate can be explained by the experimental factor $e^{-E/RT}$ of the Arrhenius equation For example, if the activation energy E of a reaction is 24000 cal mole^{-1}, the value of $e^{-E/RT}$ at 300° K will be $e^{-24000/2\times300}$, *i.e.*, $4{\cdot}248\times10^{-8}$. If the temperature is raised by 10°, then the value at 310° K will be $e^{-24000/2\times310}$ *i.e.*, $15{\cdot}56\times10^{-18}$. Thus, the increase of 10° in the temperature increases the value of the factor by about 3·6 times. This increase is due to the fact that by raising the temperature, the proportion of activated molecules increases and as a result of this, the reaction rate increases.

The Role of Activation Energy in Chemical Reaction and the Activated Complex

To understand the physical meaning of activation energy, let us suppose that a car goes from a place A to a place B. The road crosses a hill at an attitude of about 1000 feet as shown in Fig 3·9. If the engine of the car is weak then it will not be possible for the car to climb up the slope of the hill all the way to reach the top X

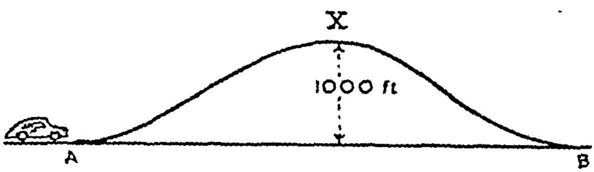


Fig. 3·9 Crossing the Hill between A and B

and then go down the other side of the hill. It will go only a part way up, stop and turn back. On the other hand, if the engine is powerful enough to surmount 1000 feet hill, it will certainly pass the barrier X and reach the place B.

This physical situation resembles with the picture of chemical reaction. When two molecules collide momentarily an intermediate aggregate made up of these two molecules is formed which afterwards breaks into products. The potential energy of the intermediate aggregate is greater than that of the reactants and the products. This high energy intermediate aggregate is called **activated complex** or **activated state.** The activated state is like the pass of the hill and places an **energy barrier** between the reactants and the products. Thus, only those reacting molecules which have enough energy to surmount the energy barrier, can be converted into products. The energy barrier determines the minimum energy which the reacting molecules should possess in order to react completely to form products. This minimum threshold energy is called the **activation energy.**

Thus a chemical reaction involves (*i*) the absorption of energy by the reactant molecules to get themselves activated, (*ii*) combina-

tion of the activated molecules to form activated complex, and (*iii*) the breaking of activated complex into products. The formation of activated complex is a characteristic of all the chemical changes.

The idea of activated complex can be illustrated qualitatively by a potential energy diagram, as shown in Fig. 3·10 for a reaction

$$AB+CD \rightarrow AC+BD$$

In the figure, the vertical axis represents the potential energy and the horizontal axis represents the reaction coordinate, *i.e.*, the course of reaction showing how far the reaction has gone from the initial state of reactants towards the final state of products. Let us start from left to right. Along the flat curve at the left, the molecules AB and

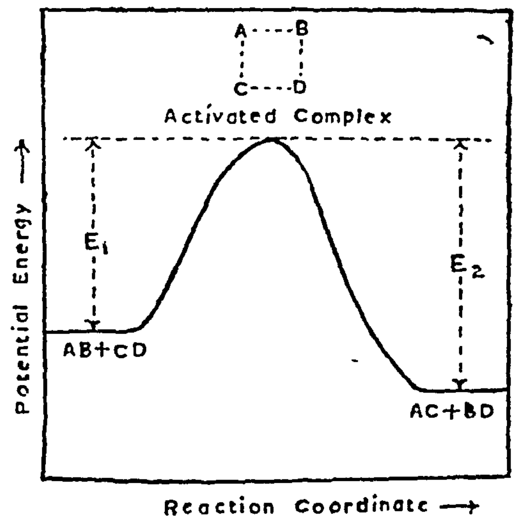


Fig. 3·10 Potential Energy Change and Activated Complex in a Chemical Reaction.

CD are approaching each other. They possess kinetic energy and because they are relatively far apart, there is no change in their total potential energy. At the beginning of the rise in curve, AB approaches ~~BC~~ more closely and the forces of repulsion between the nuclei and the electron clouds become appreciable. At this stage, the molecules are slowed down because their kinetic energies furnish the potential energy to overcome the forces of repulsion. Thus, the potential energy of the system starts increasing. The increase in potential energy continues and reaches maximum which corresponds to the activated complex. At this stage, since the potential energy of the system is maximum, the activated complex formed will be most unstable. The bonds between A—B and C—D have stretched and weakened to the extent that they are just on the point of breaking and the bonds between A—C and B—D have just started to form. Thus, the activated complex takes the geometry of most unstable

species and has approximately equal possibilities of decomposing into products or back into reactants. This can be represented as

$$\underset{\text{Reactants}}{AB+CD} \rightleftharpoons \underset{\text{Activated Complex}}{\begin{array}{ccc} A & \cdots\cdots & B \\ \vdots & & \vdots \\ C & \cdots\cdots & D \end{array}} \rightleftharpoons \underset{\text{Products}}{AC+BD}$$

If the reactants have sufficient energy to cross the energy barrier, the activated complex formed will break into the products and if they have insufficient energy to cross the barrier activated complex will break into reactants and retrace the former path. The formation of product is represented by moving down the right side of the barrier. This shows that the potential energy decreases and the flat curve represents the region where the product molecules AC and BD have separated again and the potential energy of the complex has converted into kinetic energy again.

From the above discussion it is clear that the reactants can not directly convert into products unless they cross the potential energy barrier, *i.e.*, they form the activated complex. The following are some important features of the **activated complex** :

(*i*) The activated complex is produced by the collision of reacting molecules possessing energy at least equal to the activation energy.

(*ii*) The activated complex may be regarded as a single molecule with loose bonds.

(*iii*) The potential energy of the activated complex is maximum.

(*iv*) The activated complex has transient existence only and transforms into products at a definite rate. It may also decompose into reactants back.

(*v*) In terms of activated complex a reaction is said to be unimolecular, bimolecular or termolecular depending on whether one, two, or three reacting molecules are required to form the activated complex.

(*vi*) The breaking of activated complex is essentially a unimolecular process.

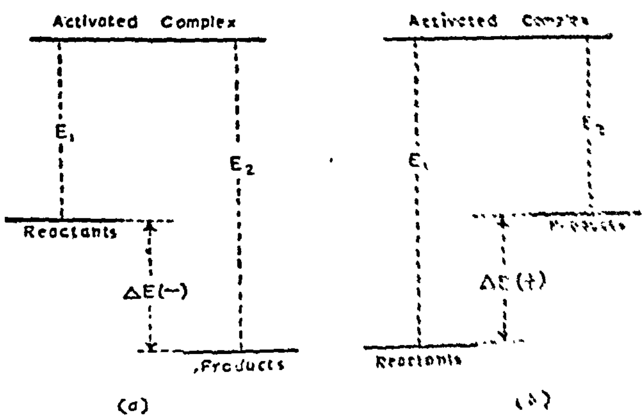
The role of activation energy in chemical reaction is that it is utilized in the weakening or breaking of bonds, forcing reacting molecules very close to one another by overcoming the forces of repulsion due to atomic nuclei and electron cloud, or feeding energy to a vibrating molecule so that its collision may result in a chemical reaction. The activation energy is the chief factor which determines whether a reaction is fast or slow at a given temperature. If the energy of activation is high, only a few molecules will possess it and

hence the reaction will be slow. When the temperature is raised, more molecules will be in activated state and hence the rate of the reaction will increase. On the other hand, if the activation energy is low, more molecules will possess it at the given temperature and the reaction will be faster.

It is clear from Fig. 3·10, that the process of activation is endothermic and the activation energy is always positive. The comparative values of the energy of activation of products and reactants determine whether the reaction is exothermic or endothermic. In the figure, E_1 represents the energy of activation of reactants and E_2 of products. The energy change in the overall reaction can be given as

$$\begin{array}{lrcll} & \text{Reactants} & \rightarrow & \text{Activated complex ;} & \Delta E = E_1 \\ & \text{Activated complex} & \rightarrow & \text{Products ;} & \Delta E = -E_2 \\ \hline \text{On adding,} & \text{Reactants} & \rightarrow & \text{Products ;} & \Delta E = (E_1 - E_2) \end{array}$$

Thus, if $E_2 > E_1$, the value of ΔE is negative and the reaction will be **exothermic**. If $E_1 > E_2$, the value of ΔE is positive and the reaction will be **endothermic**. This can be seen in Fig. 3·11 which depicts the difference in the activation energies of products and reactants



Eig. 3·11. Activation Energy in (*a*) Exothermic Process and (*b*) Endothermic Process.

for exothermic and endothermic reactions. It is evident from Fig. 3·11 (*b*), that in an endothermic process, the energy of activation must be at least equal to the heat of reaction. This is for this reason that highly endothermic processes are very slow and speed up only at higher temperatures.

Though Arrhenius theory helps in understanding the reaction process, yet it is a qualitative theory because it is unable to predict the values of E and A. Further development of the theories of reaction rates is beyond the scope of this book.

Activation Energy and Catalysts. The rate of reaction can be incressed by the addition of a suitable catalyst. The catalyst actually changes the path or mechanism of the reaction and provides a different activation energy barrier which has a lower value than the value of the barrier when the reaction is allowed to proceed uncatalysed as shown in Fig. 3·12. Since the new path has a lower energy

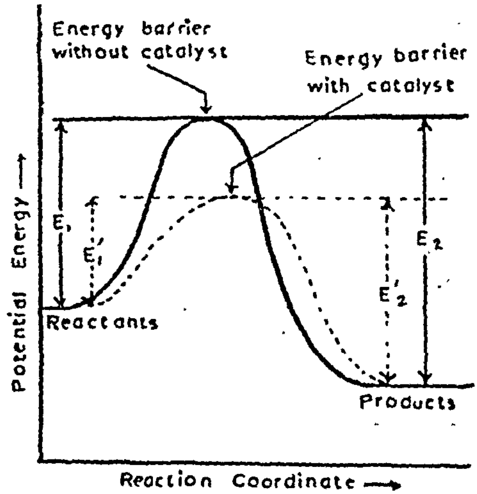


Fig. 3·12. Potential Energy Change in a Chemical Reaction with and without Catalyst

barrier, it is evident that more reacting molecules can surmount the barrier and hence the rate of reaction increases. It is to be noted that the activation energy of the products also decreases equally and, therefore, it explains the experimental fact that a catalyst has equal effect on the forward and the reverse reactions.

TEST YOUR KNOWLEDGE

1. **Complete the following.**

(i) $v = \pm \frac{dc}{\cdots}$

(ii) $k_1 = \frac{2 \cdot 303}{\cdots\cdots} \log_{10} \frac{a}{a-x}$

(iii) $c_t = c_0 \, e^{\cdots}$

(iv) $k_2 = \frac{1}{t} \frac{\cdots\cdots}{a(a-x)}$

(v) $k_2 = \frac{2 \cdot 303}{t\cdots\cdots} \log_{10} \frac{b(a-x)}{a(b-x)}$

(vi) $k_3 = \frac{1}{2t} \left[\frac{\cdots\cdots\cdots}{a^2(a-x)^2} \right]$

(*vii*) $k_n = \frac{1}{t\ldots}\left[\frac{1}{(\ldots)^{n-1}} - \frac{1}{a^{n-1}}\right]$

(*viii*) $t_2/t_1 = \log_{10}[\ldots]^{n-1}$

(*ix*) $k = A\,e^{\cdots}$

(*x*) $\log_{10}\frac{k_2}{k_1} = \frac{\ldots\ldots}{2{\cdot}303R}\left[\frac{T_2-T_1}{T_1\,T_2}\right]$

2. Fill in the blanks with appropriate words :

(*i*) The rate of reaction is given by the derivative of concentration with respect to......

(*ii*) The......elementary process determines the rate of reaction.

(*iii*) The differential rate equation shows the dependence of.........on the concentration of the reactants.

(*iv*) The integrated rate equation shows the dependence of ...... on time.

(*v*) The half life period of ...... order reaction is independent of the initial concentration of the reactant.

(*vi*) Lit mole^{-1} sec^{-1}, sec^{-1}, and lit^{-2} mole^{-2} sec^{-1} are the units of ......, ..., and ...... order reactions respectively.

(*vii*) The activated complex is produced by the collision of reacting molecules possessing energy at least equal to the......

(*viii*) The potential energy of the activated complex is......

(*ix*) ...... lowers the energy barrier.

(*x*) ......may be integral, fractional or zero but the molecularity is always a positive......

3. Give a term for each of the following :

(*i*) Equations showing quantitative weight relationships.

(*ii*) The branch of chemistry which deals with the reaction rates and reaction mechanism.

(*iii*) The rate of reaction when the concentration of reactants is unity.

(*iv*) The sum of the powers to which the concentration terms are raised in the experimentally determined rate equation.

(*v*) The number of molecules, atoms, or radicals taking part in an elementary reaction.

(*vi*) The reaction whose rate is independent of the reactant concentration.

(*vii*) The ratio of the rate constants at a temperature difference by 10°.

(*viii*) The high energy intermediate aggregate formed by the collision of activated reacting molecules.

(*ix*) The minimum amount of excess energy required by the reacting molecules to react.

(*x*) The time required to decompose half of the original substance.

KEY

1. (*i*) dt, (*ii*) t, (*iii*) $-k_1t$, (*iv*) x, (*v*) $(a-b)$, (*vi*) $x(2a-x)$. (*vii*) $n-1$, $a-x$ (*viii*) a_1/a_2, (*ix*) $-E/RT$, (*x*) E.

2. (*i*) time, (*ii*) slowest, (*iii*) rate of reaction, (*iv*) reactant concentration, (*v*) first, (*vi*) second, first, third. (*vii*) activation energy, (*viii*) maximum, (*ix*) Catalyst, (*x*) Order, integer.

3. (*i*) Stoichiometric equations, (*ii*) Chemical kinetics, (*iii*) specific reaction rate or rate constant, (*iv*) Order of reaction, (*v*) molecularity, (*vi*) Zero–order reaction, (*vii*) Temperature coefficient, (*viii*) Activated complex, (*ix*) Activation energy, (*x*) Half-life period.

QUESTIONS

1. Explain the term 'reaction rate'. Describe how it is measured. What are the factors which influence the rate of a reaction ?

2. What do you understand by (*i*) reaction rate and (*ii*) specific reaction rate ? When do they become equal ? What are their dimensions ?

3. If a reaction obeys the rate law :

$$\text{rate} = k\,[A]^{1/3}\,[B]^{1/2}$$

what are the units of k if the reaction occurs :
(*i*) in solution and (*ii*) in gas-phase.
[Ans. (*i*) mole $^{1/6}$ lit$^{-1/6}$ sec^{-1}, (*ii*) mm$^{-1/6}$ sec^{-1}]

4. If the concentrations are expressed in moles/litre and time in minutes, what are units of the specific reaction rates for (*i*) first-order, (*ii*) second-order; and (*iii*) third-order reactions ?
[Ans. (*i*) min^{-1}, (*i*) lit mole^{-1} min^{-1}, and (*iii*) lit^{2} mole^{-2} min^{-1}]

5. Distinguish clearly between the molecularity and the order of a reaction. Give suitable examples.

6. What are differential and integrated rate equations ? Derive two forms of the intergated equations for a first-order reaction.

7. The rate determining step in a hypothetical reaction is $2A + B \rightarrow C + D$. What would be the effect on the reaction rate if (*i*) the concentration of A is doubled, and (*ii*) the concentration of B is doubled ?

8. What is meant by the order of reaction ? Derive integrated rate equation for second-order reaction when the initial concentrations of both the reactants are (*i*) equal and (*ii*) unequal.

9. Give all possible integrated rate equations for a third-order reaction.

10. What is meant by the half-life period ? How the half life period is related to the initial concentration of the reactions in first, second, and third-order reaction.

11. What is meant by the energy of activation ? Discuss its role in the chemical reaction.

12. Explain the terms 'activated complex'. What are its various features.

13. Write a short account of the role of catalyst in a chemical reaction with special reference to the activation energy.

14. Discuss the influence of temperature on the reaction velocity in the light of Arrhenius theory. How is the activation energy of a chemical reaction determined ?

15. Write notes on :
(*i*) Temperature coefficient
(*ii*) Arrhenius theory
(*iii*) Zero-order reaction.

16. Giving suitable examples. show that how the knowledge of order and molecularity is helpful to know the mechanism of a chemical reaction.

17. Enumerate the various methods for determining the order of reaction. and discuss one of them in detail.

18. The decomposition of N_2O_5 in the gaseous state, a first-order reaction. is 14·8% complete in 20 minutes at 35°C. Calculate the rate constant for the reaction. What percentage would be decomposed at the end of 50 minutes? [Ans. 0·0080 min^{-1}; 32·93%]

19. The following data were obtained for the decomposition of ethylamine at 500°C.

Time (min)	0	2	6	10
Pressure (mm Hg)	55	64	79	89

Show that the reaction is of first-order, and calculate the average reaction rate. [Ans. $9·375 \times 10^{-2}$ min^{-1}]

20. Ethyl acetate was subjected to hydrolysis in normal HCl at 25°C. 5 ml of the mixture were withdrawn and titrated against standard NaOH solution at different intervals with the following results:

t (min)	0	20	75	120	175	∞
titre (ml)	20·25	21·70	25·20	27.65	30·20	43·95

Show that the reaction is of the first-order and evaluate the average value of specific reaction rate. [Ans. $3·125 \times 10^{-3}$ min^{-1}]

21. For the inversion of sucrose in presence of dil HCl, the following polarimeter readings (θ) at various times *t* were obtained

t (sec)	0	1035	3013	4857	9231	∞
θ (°)	11·20	10·35	8·87	7·64	5·19	—3·37

Show that the reaction is of first-order and calculate the average specific reaction rate. [Ans. $5·773 \times 10^{-5}$ sec^{-1}]

22. Following data were obtained in a decomposition of H_2O_2 when equal volumes of the decomposition mixture were titrated against standard $KMnO_4$ solution at regular interval

Time (min)	0	10	20	30
Volume of $KMnO_4$ (cc)	25	16·2	10·5	6·8

Show that it is a unimolecular reaction and calculate the average reaction rate. [Ans. $4·339 \times 10^{-2}$ min^{-1}]

23. Nitrogen pentoxide when allowed to decompose in CCl_4 at 45°C gave the following volumes of oxygen :

Time (min)	0	5	10	15	∞
Volume of O_2 (cc)	0	3·42	6·30	8·95	35·75

Show that the reaction is of first-order and evaluate the rate constant. [Ans. $1·959 \times 10^{-2}$ min^{-1}]

24. A second-order reaction, where $a=b$, is 20% completed in 500 seconds. How long will it take the reaction to go to 60% completion ? [Ans. 3000 sec]

25. In the study of dimerization of gaseous butadiene, the following data were obtained :

Time (sec)	0	180	460	858	1473	∞
Pressure (mm Hg)	632·0	618·5	599·4	576·1	546·8	3·16

Show that the reaction is of second-order and evaluate the average rate constant. [Ans. $3·952 \times 10^{-7}$ sec^{-1}]

26. When ethyl acetate is saponified with NaOH, the progress of the reaction can be measured by titrating the unchanged alkali against a standard acid at certain intervals. Using equal concentrations of ester and alkali, the following results were obtained in an experiment :

t (min)	0	5	25	35	55	∞
ml of acid $(a-x)$	16	10·4	4·3	3·4	2·3	0

Show that the reaction is of second order and calculate the average rate constant. What fraction of ethyl acetate will be decomposed in 30 minutes ? [Ans. $6{\cdot}730 \times 10^{-3}$ ml mole^{-1} min^{-1}, 0·7638]

27. The following data refer to the decomposition of gaseous acetaldehyde at 518°C.

Initial pressure (mm)	400	300	200
Half-life period (sec)	370	495	745

Determine the order of reaction. [Ans. 2]

28. The activation energy of a reaction is 20000 cal mole^{-1}. Calculate the ratio of the two rate constants at 273° and 373°K. [Ans. $1{\cdot}954 \times 10^4$]

29. The following values have been obtained of the rate constants for the decomposition of N_2O_5 at various temperatures :

Temperature (°c)	0	25	35	45	55	65
k (sec^{-1})	$4{\cdot}7 \times 10^{-4}$	$0{\cdot}34 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	$4{\cdot}98 \times 10^{-4}$	$15{\cdot}0 \times 10^{-4}$	$48{\cdot}7 \times 10^{-4}$

Determine the activation energy graphically.

30. The rate constants for the decomposition of acetaldehyde at 460° and 592°K were found to be 0·035 and 4·96 moles lit^{-1} sec^{-1}. Calculate the activation energy of the reaction.

[Ans. 20310 cal mole^{-1}]

4

Thermodynamics

(THE SECOND LAW, ENTROPY, AND FREE ENERGY)

Introduction

The first law of thermodynamics deals with the conservation of energy and establishes quantitative relation between different kinds of energy. It gives the total energy change in a chemical reaction but fails to give answer to the following questions : Will a particular process at all occur ? What will be the direction and extent of the process ? For example, heat flows from a hot body A to a cold body B when both are brought in contact with each other. The first law states that the heat lost by body A is equal to the heat gained by body B. It never indicates that heat can only flow from hot body A to cold body B and not in the reverse direction *i.e.*, from B to A. Thus, we see that the first law is inadequate to predict the direction of a certain process to occur. To predict the direction of change we should have a knowledge of some other criterion except the first law. The second law of thermodynamics provides the criterion for predicting the direction and extent of a particular change. Any approach which leads to the criterion for the direction of occurrence of a process becomes the basis of the second law. Different scientists attacked this problem in different ways and it is for this reason we find a good variety of statements of the second law. All these statements of the second law though appear to be different but they ultimately lead to the same aim, *i.e.*, predict the direction of the occurrence of a process.

Spontaneous processes

Processes taking place in a system without the assistance of any external agency are termed as **natural** *or* **spontaneous processes**. Thus, in a spontaneous process no external work is done on the system. The following are some examples of spontaneous processes :

(*i*) The flow of water from a higher level to a lower level. The flow of water continues until the levels become equal, *i.e.*, mechanical equlibrium is attained.

(*ii*) Expansion of a gas from a region of higher pressure to a region of lower pressure. The expansion will continue until the pressures become equal, *i.e.*, mechanical equilibrium is, attained.

(*iii*) Flow of heat from a hotter body to a colder body. The flow will continue until the temperatures become equal, *i.e.*, thermal equilibrium is attained.

(*iv*) When a zinc rod is placed in contact with the solution of copper sulphate, zinc dissolves and cupric ions are reduced to copper metal which deposits on the zinc rod. This occurs spontaneously and continues until chemical equilibrium is reached.

From these examples it is evident that spontaneous processes take place in one direction only and proceed towards a state of equilibrium. It is a matter of common experience that spontaneous processes can not be reversed by themselves. Thus, water cannot move from lower to higher level; gases cannot flow from a region of low pressure to a region of high pressure; heat cannot flow from a colder to a hotter body, dissolved zinc cannot be precipitated back from the solution of zinc sulphate and copper. Spontaneous processes may, however, be reversed with the help of some external assistance *i.e.*, when energy from outside is supplied. Thus, water can be lifted from a lower to an upper level with the help of a pump. Gas molecules can be made to move from a region of low pressure to a region of high pressure by applying pressure on them. Heat can be made to flow from a colder to a hotter body by doing external work on the system, *e.g.*, refrigerator. Zinc can be obtained back from the solution of zinc sulphate and copper by doing electric work on the system. From these examples, it may be concluded that *spontaneous processes are irreversible and can be reversed only when work is done on the system.*

Another aspect of spontaneous process is that no useful work is obtained when it is allowed to occur by itself. For example, when a gas is allowed to expand in vacuum no work is obtained. However, useful work may be obtained from spontaneous processes by introducing a suitable mechanism. Thus, flow of water from a higher to a lower level can yield work if a turbine is employed. The flow of heat from a hotter to a colder body can produce work with the help of a heat engine. The expanding gas can move a piston. Useful work from the reaction between zinc and copper sulphate can be obtained through a galvanic cell. It should be borne in mind that maximum amount of work can be obtained from a spontaneous process if it is carried out reversibly. For example, in spontaneous expansion of a gas, maximum work could be obtained if it is allowed to expand against a piston, the pressure on which is just infinitesimally smaller than the pressure of the gas. This is reversible expansion because the process can be reversed by increasing the pressure on the piston by an infinitesimally small amount.

General Statements of the Second Law of Thermodynamics

As already stated that the second law of thermodynamics may be stated in a great variety of ways. Unfortunately, the second law cannot be stated with the same precision and simplicity as the first law. No single statement can give its full meaning. A few commonly quoted statements are given below :

(*i*) *Heat can flow spontaneously from a hotter to a colder body*, alternatively, *heat cannot flow from a colder to a hotter body without the intervention of some external energy.*

(*ii*) *All natural or spontaneous processes tend to go to a state of equilibrium.*

(*iii*) *All natural or spontaneous processes are irreversible.*

(*iv*) *All natural or spontaneous processes can be made to yield work but the maximum work can only be obtained if the process is carried out reversibly.*

(*v*) *It is impossible to convert heat completely into an equivalent amount of work without producing changes in some part of system or surroundings.*

The first four statements are based on the examples of spontaneous process as discussed in the last section. The statement (*v*) needs explanation. It is a matter of common experience that every form of energy has a natural tendency to be converted into heat but heat shows no natural tendency to be converted into any other form. Thus, if heat is to be converted into work some external agency, such has heat engine, is to be employed. Even then the complete conversion of heat into work is not possible, only a fraction of heat is converted into an equivalent amount of work. Work can be obtained when heat is transferred from a body at a higher temperature to a body at a lower temperature, because such a process can take place spontaneously. This is the principle of heat engine. The engine takes heat from the 'source' at a higher temperature, a part of the heat absorbed is converted into an equivalent amount of work and the rest is given up to the 'sink' at a lower temperature. *The fraction of the absorbed heat converted into an equivalent amount of work is known as the* **efficiency** *of the engine.* No engine has yet been devised which has 100 percent efficiency. Thus, complete conversion of heat into work is not possible. Further, suppose in an engine ideal gas is filled in the cylinder fitted with piston; when heat is absorbed, the gas expands and exactly an equivalent amount of work is done against the piston. In this case heat is converted into work but at the same time the volume of the gas has increased. Thus, heat cannot be converted completely into work without producing changes elsewhere.

The statements of the second law as given above cann... conveniently applied to chemical problems. The main aim ... second law is to establish a criterion which can determine ...

or not a chemical or physical change occurs spontaneously. Since spontaneous processes generally occur with the decrease in energy of the system, at one time chemists believed that chemical reactions proceed spontaneously in the direction of heat evolution or in other words, only exothermic reactions are spontaneous. This conclusion is wrong because there are many endothermic reactions which do occur spontaneously. So it is evident that energy alone is inadequate in deciding the spontaneity of a process.

Now it has become important to obtain a function which as a consequence of second law should serve as criterion of spontaniety The function should be a state function, *i.e.*, its value should depend on the state of the system and not on the path of the process. Further, it should change in a particular manner, *e.g.*, always increase as the process occurs spontaneously. A function which fulfils these conditions has been introduced and given the name **entropy.**

ENTROPY

Entropy in denoted by S. It is defined in terms of differential equation for dS, the infinitesimal small change in entropy. If dq_{rev} is the amount of heat absorbed by the system in a reversible manner at a constant temperature T, then the entropy change dS is given by

$$dS = \frac{dq_{rev}}{T} \qquad ...(4{\cdot}1)$$

For finite changes

$$\triangle S = \frac{q_{rev}}{T} \qquad ...(4{\cdot}2)$$

Thus, **entropy change** may be defined as *the amount of heat absorbed by the system in a reversible manner divided by the absolute temperature at which the heat is absorbed.*

Entropy is a State Function. In the definition of entropy the quantity q_{rev} is not a state function and depends on the path of the change. There may be number of ways in which the process can be performed reversibly and in each case the value of q_{rev} will be different. Hence dq_{rev} is not a perfect differential. However, dq_{rev}/T is a perfect differential. This can be shown in the following way :

Suppose 1 mole of an ideal gas is undergoing a reversible expansion. From the first law

$$dq_{rev} = dE + PdV$$

$$= C_v dT + \frac{RT}{V} dV$$

or

$$\int dq_{rev} = \int C_v \, dT + \int \frac{RT}{V} dV \qquad ...(4{\cdot}3)$$

we know that dq_{rev} is not an exact differential, hence it cannot be integrated. This is confirmed by observing the right-hand side of

Eq. (4·3), where the quantity $\int \frac{RT}{V}\,dV$ cannot be evaluated unless we specify the path, or in other words, the relation between T and V is known. For different values of T, V will have different values. Thus dq_{rev} depends on the path by which the expansion is carried out. Now dividing Eq. (4·3) by T on both the sides, we get

$$\int \frac{dq_{rev}}{T} = \int \frac{C_V}{T} dT + \int \frac{RT}{V} \frac{1}{T} dV$$

$$= \int \frac{C_V}{T} dT + \int \frac{R}{V} dV$$

$$= C_V \ln T + R \ln V + \text{constant} \qquad \text{...(4·4)}$$

It follows that $\int \frac{dq_{rev}}{T}$ can be evaluated, hence $\frac{dq_{rev}}{T}$ is an exact differential. It may, therefore, be concluded that entropy change dS is an exact or perfect differential and hence entropy S is a state function.

Thus, if a system changes from initial state 1 to final state 2, the entropy change is expressed by integrating Eq. (4·1) between the limits of initial state 1 and final state 2,

$$\int_1^2 dS = \int_1^2 \frac{dq_{rev}}{T}$$

or

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T} \qquad \text{...(4·5)}$$

where S_1 and S_2 are the entropies of the system in the initial and final states respectively.

It should be clearly borne in mind that the entropy change dS is equal to the amount of heat absorbed divided by the absolute temperature only when the process is carried out reversibly. If the process is carried out irreversibly the quantity of heat absorbed dq_{irrev} divided by temperature T *i.e.*, dq_{irrev}/T will not be equal to dS, the change in the entropy, because

$$\frac{dq_{rev}}{T} \neq \frac{dq_{irrev}}{T}$$

The amount of heat absorbed in irreversible manner will be indefinite and uncertain and hence cannot be used in evaluating the entropy changes.

From Eq. (4.1) it is evident that when heat is absorbed by the system dq is positive and hence dS is also positive. Thus, the entropy of the system increases with the absorption of heat and decreases

with the evolution of heat. In an adiabatic reversible change, where $dq_{rev}=0$, the entropy change dS is also zero. Hence adiabatic reversible processes are associated with no entropy change and are called **isoentropic processes.**

Units of Entropy. Entropy has dimensions of **energy×temperature⁻¹** and is generally expressed in **cal deg^{-1}.** It is also referred to as **entropy unit** or **eu.** Thus, 1 eu = 1 cal deg^{-1}.. Entropy also depends on the amount of the substance, hence the amount should also be specified in the units. For 1 mole of a substance the units of entropy are **cal deg^{-1} mole^{-1}.** This is called **molar entropy.** For 1 gm of a substance the entropy units are **cal deg^{-1} gm^{-1}.**

Entropy calculations

Entropy is a state function and the change in entropy for a given process is independent of the path between the initial and the final states. The process may occur by any path, reversible or irreversible, but the entropy change will be the same. To compute the value of ΔS, a path for which a calculation is as simple as possible is chosen. The most convenient path frequently chosen is the reversible path, because Eq. (4·1) is applicable to reversible processes and employed in entropy change calculations.

(*i*) **Entropy changes for an Ideal Gas.** Consider a system consisting of n moles of an ideal gas occupying a volume V at a pressure P and temperature T. If dq_{rev} amount of heat is absorbed by the system reversibly, then the increase in entropy dS is given by

$$dS=\frac{dq_{rev}}{T} \qquad ...(4\cdot6)$$

From the first law of thermodynamics, for a reversible process in which only pressure-volume work is involved

$$dq_{rev} = dE+PdV \qquad ...(4\cdot7)$$

Substituting for dq_{rev} from Eq. (4·7) in Eq. (4·6), we get

$$dS=\frac{dE+PdV}{T} \qquad ...(4\cdot8)$$

For n moles of an ideal gas, we know that

$$P = \frac{nRT}{V}$$

and $$dE = nC_v dT$$

where C_v is the molar heat at constant volume. Substituting these values of P and dE in Eq. (4·8), we get

$$dS = \frac{nC_V dT + (nRT/V)dV}{T}$$

or $$dS = nC_V \frac{dT}{T} + nR\frac{dV}{V} \qquad ...(4\cdot9)$$

If the entropy, volume and temperature of the system in the initial state are S_1, V_1 and T_1 and in the final state are S_2, V_2 and T_2 respectively, then integrating Eq. (4·9) between these limits we get

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + \int_{V_1}^{V_2} nR\frac{dV}{V}$$

Assuming C to be independent of temperature over the temperature range considered, we obtain

$$\Delta S = S_2 - S_1 = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \qquad ...(4\cdot10)$$

For 1 mole of an ideal gas

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \qquad ...(4\cdot11)$$

An alternate form of Eq. (4·10) involving pressure terms can be obtained in the following manner :

If P_1 is the pressure of the system in the initial state and P_2 in the final state, then from the gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

or $$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$$

Substituting in Eq. (4·10), we obtain

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1T_2}{P_2T_1}$$

$$= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$= n(C_V + R) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Since $(C_V + R) = C_P$, hence

$$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \qquad ...(4\cdot12)$$

From Eq. (4·10) and (4·12) entropy changes for an ideal gas can be calculated. These equations take different forms under different conditions.

(*i*) **For an Isothermal Process** *i.e.* when $T_1 = T_2$. For these processes Eqs. (4·10) and (4·12) are reduced to

$$\Delta S_T = nR \ln \frac{V_2}{V_1} \quad ...(4.13)$$

and $$\Delta S_T = nR \ln \frac{P_1}{P_2} \quad ...(4.14)$$

The subscript T in ΔS_T indicates that the process is occurring at constant temperature. In an expansion $V_2 > V_1$ or $P_1 > P_2$, hence ΔS_T is positive but in contraction $V_1 > V_2$ or $P_2 > P_1$ and hence ΔS_T is negative. From this it is concluded that in an isothermal expansion entropy increases and in contraction it decreases.

(*ii*) **For an Isobaric Process** *i.e.*, when $P_1 = P_2$. For such process Eq. (4.12) reduces to

$$S_p = nC_p \ln \frac{T_2}{T_1} \quad ...(4.15)$$

(*iii*) **For an Isochoric Process** *i.e.*, when $V_1 = V_2$. For such a process Eq. (4.10) reduces to

$$\Delta S_V = nC_V \ln \frac{T_2}{T_1} \quad ...(4.16)$$

Example 1. *Calculate the entropy change when 2 moles of an ideal gas are allowed to expand from a volume of 1 litre to a volume of 10 litres at 27°C.*

Solution. We know that for an isothermal expansion of an ideal gas

$$\Delta S_T = nR \ln \frac{V_2}{V_1} = 2.303\, nR \log_{10} \frac{V_2}{V_1}$$

Here $V_1 = 1$ lit

$V_2 = 10$ lit

$n = 2$ moles

$R = 1.987$ cal deg^{-1} mole^{-1}

$$\therefore \Delta S_T = 2.303 \times 2 \times 1.987 \log_{10} \frac{10}{1}$$

$$= 9.152 \text{ cal deg}^{-1}$$

Example 2. *Calculate the entropy change when 1 mole of an ideal gas is heated from 20°C to 40°C at a constant pressure. The molar heat at constant pressure of the gas over this temperature range is 6.189 cal deg^{-1}.*

Solution. We know that for an isobaric process

$$\Delta S_P = nC_P \ln \frac{T_2}{T_1} = 2.303\, nC_P \log_{10} \frac{T_2}{T_1}$$

Here $n = 1$ mole

$C_P = 6.189$ cal deg^{-1}

$$T_1 = 273+20 = 293°K$$
$$T_2 = 273+40 = 313°K$$

$$\therefore \Delta S_P = 2{\cdot}303 \times 1 \times 6{\cdot}189 \times \log_{10} \frac{313}{293}$$
$$= 0{\cdot}4077 \text{ cal deg}^{-1}.$$

Example 3. *Calculate the entropy change when 5 moles of an ideal gas are allowed to expand isothermally at 20°C from a pressure of 10 atm to a pressure of 2 atm.*

Solution. We know that for an isothermal expansion involving pressure changes

$$\Delta S_T = nR \ln \frac{P_1}{P_2} = 2{\cdot}303\, nR \log_{10} \frac{P_1}{P_2}$$

Here $P_1 = 10$ atm
$P_2 = 2$ atm
$n = 5$ moles
$R = 1{\cdot}987$ cal deg^{-1} mole^{-1}

$$\therefore \Delta S_T = 2{\cdot}303 \times 5 \times 1{\cdot}987 \times \log_{10} \frac{10}{2}$$
$$= 16 \text{ cal deg}^{-1}$$

Example 4. *Calculate the entropy change when 3 moles of an ideal gas ($C_V = 7{\cdot}88$ cal deg^{-1} mole^{-1}) are heated from a volume of 200 lit at 50°C to a volume of 300° lit at 150°C.*

Solution. We know that

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$
$$= 2.303\, n\, C_V \log_{10} \frac{T_2}{T_1} + 2{\cdot}303\, nR \log \frac{V_2}{V_1}$$

Here $n = 3$ moles,
$C_V = 7.88$ cal deg^{-1} mole^{-1}
$R = 1{\cdot}987$ cal deg^{-1} mole^{-1}
$T_1 = 273+50 = 323°K$
$T_2 = 273+150 = 423°K$
$V_1 = 200$ lit
$V_2 = 300$ lit

$$\Delta S = 2{\cdot}303 \times 3 \times 7{\cdot}88 \times \log_{10} \frac{423}{323} + 2{\cdot}303 \times 1{\cdot}987 \times 3 \times \log \frac{300}{200}$$
$$= 6{\cdot}375 + 2{\cdot}417$$
$$= 8{\cdot}792 \text{ cal deg}^{-1}$$

Example 5. *Calculate the entropy change involved in expanding 1 mole of an ideal gas from 15 litres at 2 atm pressure to 50 lit at 1 atm pressure. ($C_P = 7{\cdot}4$ cal deg^{-1} mole^{-1})*

Solution. We know that

$$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$
$$= 2{\cdot}303\, nC_P \log_{10} \frac{T_2}{T_1} + 2{\cdot}303\, nR \log_{10} \frac{P_1}{P_2}$$

Here
$$n = 1 \text{ mole}$$
$$C_p = 7{\cdot}4 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$R = 1{\cdot}987 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$P_1 = 2 \text{ atm}$$
$$P_2 = 1 \text{ atm}$$

For an ideal gas $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

or $$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \frac{50\times 1}{15\times 2} = \frac{5}{3}$$

$$\therefore \Delta S = 2{\cdot}303\times 1\times 7{\cdot}4\times \log_{10}\frac{5}{3} + 2{\cdot}303\times 1\times 1{\cdot}987\times \log_{10}\frac{2}{1}$$
$$= 3{\cdot}779 + 1{\cdot}377$$
$$= 5{\cdot}156 \text{ cal deg}^{-1}.$$

(2) Entropy Change in Heating a Solid or a Liquid. When a solid or a liquid is heated without producing change in state, the heat change is given by

Quantity of heat absorbed = Mass × Specific heat × Temperature rise
= No. of moles × Molar heat × Temperature rise.

Thus, if m gm of a solid or a liquid of specific heat s is heated reversibly through temperature dT, the amount of heat absorbed is given by

$$dq_{rev} = ms\,dT$$

$$\therefore \text{ The entropy change } dS = \frac{dq_{rev}}{T} = \frac{msdT}{T}$$

or $$\Delta S = \int_{T_1}^{T_2} \frac{msdT}{T} \qquad \ldots(4{\cdot}17)$$

Assuming that s remains constant within the temperature limits T_1 and T_2, Eq. (4·17) on integration gives

$$\Delta S = ms \ln\frac{T_2}{T_1} = 2{\cdot}303\ ms \log_{10}\frac{T_2}{T_1} \qquad \ldots(4{\cdot}18)$$

Example 6. *Calculate the change in entropy when 2 moles of lead are heated from 27°C to 28°C. The specific heat of lead over this temperature range is 0·03 cal. gm⁻¹ and the atomic weight of lead is 207.*

Solution. We know that

$$\Delta S = 2{\cdot}303\ ms \log_{10}\frac{T_2}{T_1}$$

Here
$$m = 2\times 207 = 414 \text{ gm}$$
$$s = 0{\cdot}03 \text{ cal gm}^{-1}$$
$$T_1 = 273+27 = 300^\circ K$$
$$T_2 = 273+28 = 301^\circ K$$

$$\therefore \Delta S = 2{\cdot}303\times 414\times 0{\cdot}03\times \log_{10}\frac{301}{300}$$
$$= 0{\cdot}0428 \text{ cal deg}^{-1}.$$

Entropy Change Accompanying Change of Phase. A process of change of state *e.g.*, melting of solid or vaporization of liquid may be carried out at constant temperature reversibly as the two phases are in equilibrium for all times during the change. Suppose the process of change of state of 1 mole of substance is carried out reversibly, the amount of heat absorbed will be equal to the molar heat of fusion or vaporization and the temperature will be the melting or boiling point. Thus, the molar entropy change accompanying a fusion process is given by

$$\Delta S = \frac{L_f}{T_f} \qquad \text{...(4·19)}$$

where L_f is the molar heat of fusion and T_f is the freezing or melting point on the absolute scale. Similarly, the molar entropy change accompanying a vaporization process is given by

$$\Delta S = \frac{L_v}{T_b} \qquad \text{...(4·20)}$$

where L_v is the molar heat of vaporization and T_b is the boiling point on the absolute scale.

In the same way the molar entropy change accompanying transition of one allotrope into another is given by

$$\Delta S = \frac{L_t}{T_t} \qquad \text{...(4·21)}$$

where L_t is the molar heat of transition and T_t is the transition temperature on the absolute scale.

Example 7. *Calculate the entropy change when 1 mole of ethanol is evaporated at 351°K. The molar heat of vaporization of ethanol is 9522 cal mole*$^{-1}$.

Solution : We know that

$$\Delta S = \frac{Lv}{T_b}$$

Here $L_v = 9522$ cal mole^{-1}

$T_b = 351$°K

$$\therefore \quad \Delta S = \frac{9522}{351} = 27{\cdot}18 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Example 8. *Calculate the total entropy change when [illegible] of ice is converted into water at 0°C. The latent heat [illegible] ice is 80 cal gm*$^{-1}$.

Solution : We know that molar entropy change

$$\Delta S = \frac{L_f}{T_f}$$

Here latent heat of ice $= 80$ cal gm^{-1}

$\therefore$ Molar heat of fusion $L_f = 80 \times 18$ cal mole^{-1}

$T_f = 273°K$

$$\therefore \quad \Delta S = \frac{80 \times 18}{273} = 5{\cdot}274 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

The entropy change per mole $= 5{\cdot}274$ cal deg^{-1}

$\therefore$ The total entropy change for 5 moles $= 5 \times 5{\cdot}274$

$= 26{\cdot}37$ cal deg^{-1}

Example 9. *Calculate the total entropy change when 5 moles of ice at 0°C and 1 atm pressure is converted into steam at 100°C. The molar heat of fusion of ice and the molar heat of vaporization of water are 1440 and 9720 cal mole^{-1}. The molar heat capacity of water over this temperature range may be taken equal to 18 cal mole^{-1}.*

Solution : The process is irreversible. To compute the entropy change, the given process may be imagined to be carried out reversibly in the following three steps :

(*i*) H_2O (*s*) at 0°C $\rightarrow$ H_2O (*l*) at 0°C

(*ii*) H_2O (*l*) at 0°C $\rightarrow$ H_2O (*l*) at 100°C

(*iii*) H_2O (*l*) at 100°C $\rightarrow$ H_2O (*g*) at 100°C

The molar entropy change in process (*i*) is given by

$$\Delta S_1 = \frac{L_f}{T_f} = \frac{1440}{273} = 5{\cdot}274 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

The molar entropy change in process (*ii*) is given by

$$\Delta S_2 = 2{\cdot}303\ C_p \log_{10} \frac{T_2}{T_1}$$

$$= 2{\cdot}303 \times 18 \times \log_{10} \frac{373}{273}$$

$$= 5{\cdot}616 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

The molar entropy change in process (*iii*) is given by

$$\Delta S_3 = \frac{L_v}{T_b} = \frac{9720}{373} = 26{\cdot}06 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$\therefore$ The total molar entropy change $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$= 5{\cdot}274 + 5{\cdot}616 + 26{\cdot}06$

The entropy change per mole $= 36{\cdot}95$ cal deg^{-1} mole^{-1}

$= 36{\cdot}95$ cal deg^{-1}

$\therefore$ The total entropy change for 5 moles $= 5 \times 36{\cdot}95$

$= 184{\cdot}75$ cal deg^{-1}

Entropy Changes in Reversible Processes

To evaluate the total entropy change of the universe, the entropy change of the system as well as of the surroundings should be considered. When a system gains heat, the surroundings loses heat and hence their entropies also change. The total change in entropy will, therefore, be equal to the algebraic sum of entropy

changes of the system and the surroundings, *i.e.*,

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$

Consider an isothermal reversible expansion of an ideal gas. The gas absorbs q_{rev} heat at temperature T. The entropy change of the gas *i.e.*, system is given by

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

Since the expansion is reversible, the system is in equilibrium with its surroundings at all times during the expansion. Hence, the surroundings loses an amount of heat equal to q_{rev}, or we can say that the surroundings absorbs $-q_{rev}$ of heat. The entropy change of the surroundings is given by

$$\Delta S_{surroundings} = -\frac{q_{rev}}{T}$$

∴ The total entropy change of the universe,

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$

$$= \frac{q_{rev}}{T} - \frac{q_{rev}}{T}$$

or $$\Delta S = 0 \qquad \ldots(4{:}22)$$

It is concluded that *for a reversible process the total entropy change of the universe is zero.*

Entropy Changes in Irreversible Processes

Suppose an irreversible process is occurring at temperature T and let q_{irrev} be the amount of heat absorbed by the system from its surroundings. The total entropy change of the system ΔS_{system} will be greater than the quantity $\frac{q_{irrev}}{T}$. This can be shown as follows:

Consider a system changes from state 1 to state 2 once reversibly and again irreversibly. From the first law of thermodynamics the heat changes for the two processes may be written as

$$q_{rev} = \Delta E + w_{rev} \qquad \ldots$$

$$q_{irrev} = \Delta E + w_{irrev} \qquad \ldots$$

Since initial and final states are same, subtracting Eq. (4·2[illegible]) from (4·23), we obtain

$$q_{rev} - q_{irrev} = w_{rev} - w_{irrev}$$

we know that between the same two states the work [illegible] system in a reversible process is greater than the [illegible] versible process, *i.e.*,

$$w_{rev} > w_{irrev}$$

Applying Eq. (4·26) in Eq. (4.25), we get

$$q_{rev} - q_{irrev} > 0$$

$$\text{or} \qquad q_{rev} > q_{irrev} \qquad ...(4\cdot27)$$

Dividing Eq. (4.27) by T on both the sides, we get

$$\frac{q_{rev}}{T} > \frac{q_{irrev}}{T} \qquad ...(4\cdot28)$$

Since $\frac{q_{rev}}{T} = \Delta S_{system}$

$$\therefore \qquad \Delta S_{system} > \frac{q_{irrev}}{T} \qquad ...(4\cdot29)$$

Now we shall calculate the total entropy change of the universe in an irreversible process. When q_{irrev} amount of heat is absorbed by the system from its surroundings to carry out the process, the entropy increase of the system ΔS_{system} will be same whether the process is carried out reversibly or irreversibly, because the entropy is a state property. However, the entropy change of the surroundings does not depend on the change in the state of the system and vary with the process by which the change is brought about. The entropy change of the surroundings may be best ascertained by supposing that the initial state of the surroundings can be restored by supplying q_{irrev} amount of heat in a reversible manner at temperature T *i.e.*, by increasing the entropy of the surroundings by the amount q_{irrev}/T. Thus, in the process under consideration the entropy change of the surroundings $\Delta S_{surroundings}$ will be numerically equal but opposite in sign of the above value *i.e.*,

$$\Delta S_{surroundings} = -\frac{q_{irrev}}{T}$$

∴ The total entropy change of the universe

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$

$$= \Delta S_{system} - \frac{q_{irrev}}{T}$$

Since $\Delta S_{system} > \frac{q_{irrev}}{T}$ vide Eq. (4·29)

$$\therefore \qquad \Delta S > 0 \qquad ...(4\cdot30)$$

Thus, *in an irreversible or spontaneous process, the entropy of the universe increases.* This can be illustrated by taking the following examples :

(*i*) **Isothermal Expansion of an Ideal Gas.** Consider an irreversible isothermal expansion of an ideal gas. Suppose n moles of an ideal gas expands irreversibly from a volume V_1 to a volume

V_2. Since ΔS_{system} is independent of the path of the change, it is given by

$$\Delta S_{system} = nR \ln \frac{V_2}{V_1}$$

The entropy change of the surroundings will, however, be different. Let us take the extreme case of isothermal free expansion *i.e.*, expansion in vacuum. In this case no work is done by the gas *i.e.*, $w=0$. For an isothermal process $\Delta E = 0$. According to the first law of thermodynamics,

$$\begin{aligned} q &= \Delta E + w \\ &= 0+0 = 0 \end{aligned}$$

This shows that no heat is absorbed by the system and as such no heat will be given up by the surroundings and consequently

$$\Delta S_{surroundings} = 0$$

∴ The total entropy change of the universe

$$\begin{aligned} (\Delta S)_{universe} &= \Delta S_{system} + \Delta S_{surroundings} \\ &= nR \ln \frac{V_2}{V_1} + 0 \end{aligned}$$

or $$(\Delta S)_{universe} = nR \ln \frac{V_2}{V_1}$$

Since $V_2 > V_1$, the value of ΔS is positive. Hence in an irreversible expansion of an ideal gas the entropy of the universe increases.

(*ii*) **Flow of heat from a Higher to a Lower Temperature.** This process is irreversible. Imagine a large body A at a higher temperature T_h is brought in contact with another body B at a lower temperature T_l so that a small amount of heat q is transferred from A to B irreversibly. The bodies are imagined large enough so that the temperatures of both the bodies do not change with the gain or loss of a small amount of heat q.

To compute the entropy change, let us imagine that this process is carried out reversibly in the following manner. Suppose an ideal gas in a cylinder is first brought in contact with A at a temperature T_h and absorbs q amount of heat reversibly. The cylinder is then detached from A and the gas is allowed to expand adiabatically and reversibly until the temperature reaches T_l. Since the expansion is adiabatic, the entropy change is zero. The gas is then brought in contact with B at a temperature T_l and compressed reversibly and isothermally until q amount of heat is transferred to B. In the whole process,

the entropy change experienced by A *i.e.*, $\Delta S_A = -\frac{q}{T_h}$

and the entropy change experienced by B *i.e.,* $\Delta S_B = \frac{q}{T_l}$

$\therefore$ The total entropy change of the system

$$\Delta S = \Delta S_A + \Delta S_B$$

$$= -\frac{q}{T_h} + \frac{q}{T_l}$$

$$= \frac{q}{T_l} - \frac{q}{T_h} \qquad \ldots(4{\cdot}31)$$

Since the initial and the final states of the system are the same in the irreversible process also, the entropy change of the system in the irreversible process is still given by Eq. (4·31).

Since $T_h > T_l$

$$\therefore \Delta S = \frac{q}{T_l} - \frac{q}{T_h} > 0 \qquad \ldots(4{\cdot}32)$$

In the given process, both the bodies A and B only have undergone any change and the surroundings remain unaffected hence we can say that the irreversible process is accompanied by entropy increase of the universe.

Entropy and The Second Law of Thermodynamics

We have seen that in an irreversible process the total entropy of the system and the surroundings, *i e.,* universe increases. Since all spontaneous processes are irreversible, we can say that spontaneous processes occur with the increase in entropy. Conversely, it can be said that a process may occur spontaneously in the direction in which the entropy of the universe increases. This forms a criterion for a spontaneous change. Thus, the definition of entropy and its general behaviour constitute another expression for the second law of thermodynamics. The formal statement of the **Second Law of Thermodynamics** in terms of entropy may be given as follows :

There is a thermodynamic function, called entropy S. The change in entropy is given by $dS = dq_{rev}/T$ where dq_{rev} is the amount of heat absorbed by the system reversibly at $T°K$. In all reversible processes, the entropy of the universe remains unchanged whereas in all irreversible processes, the entropy of the universe increases.

This expression of the second law is most useful from chemist's point of view. It immediately tells us that a chemical reaction would occur spontaneously in a direction characterised by the entropy increase. The change will continue until the entropy reaches maximum as permitted by the system under consideration and finally equilibrium is established.

Physical Significance of Entropy

Now, two aspects of the entropy will be discussed which throw some light on its physical significance.

(*i*) **Entropy as a Measure of degree of Chaos or Disorder or Randomness.** We have already seen that spontaneous or natural processes gradually pass into equilibrium state. The equilibrium state is the state of maximum randomness or disorder. To illustrate this let us take an example of the mixing of two gases—hydrogen and oxygen as shown in fig. 4·1. The two gases are contained in a

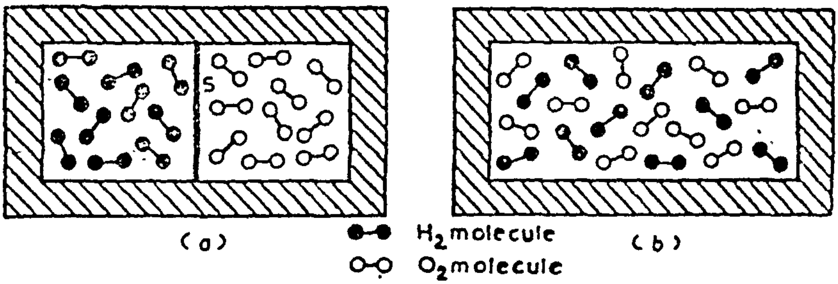


Fig. 4·1. Mixing of Two Gases.

closed container and separated by a shutter S [Fig. 4·1 *a*]. When the shutter is removed, the gases diffuse into one another spontaneously and eventually mix up as shown in Fig. 4·1 (*b*)·

What we observe in this process ? At the start, the molecules of two gases were occupied in separate compartments and after removing the shutter they diffused and become more mixed or in other words, the system has become more chaotic or disordered.

Similarly, in the dissolution of NaCl in water as shown in Fig. 4·2, we see that at the beginning, water molecules are occupied in one part of the vessel and the ions of salt in the other part. The dissolution process is spontaneous and after some time the molecules of water and ions of the salt are mixed up and the system becomes more chaotic.

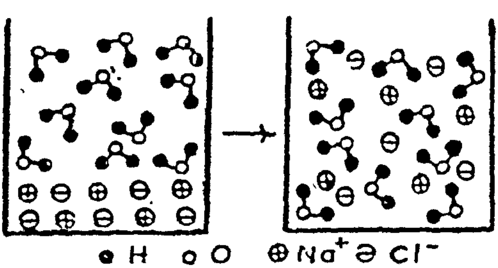


Fig. 4·2 Dissolution of NaCl in Water.

and the entropy change experienced by B *i.e.*, $\triangle S_B = \frac{q}{T_l}$

$\therefore$ The total entropy change of the system

$$\begin{aligned}\triangle S &= \triangle S_A + \triangle S_B \\ &= -\frac{q}{T_h} + \frac{q}{T_l} \\ &= \frac{q}{T_l} - \frac{q}{T_h} \qquad \ldots(4{\cdot}31)\end{aligned}$$

Since the initial and the final states of the system are the same in the irreversible process also, the entropy change of the system in the irreversible process is still given by Eq. (4·31).

Since $T_h > T_l$

$$\therefore \ \triangle S = \frac{q}{T_l} - \frac{q}{T_h} > 0 \qquad \ldots(4{\cdot}32)$$

In the given process, both the bodies A and B only have undergone any change and the surroundings remain unaffected hence we can say that the irreversible process is accompanied by entropy increase of the universe.

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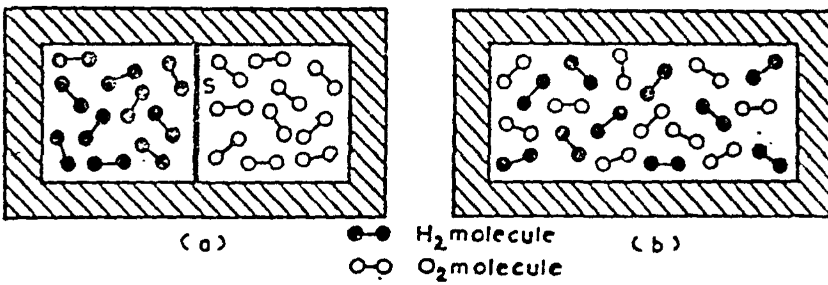

Fig. 4·1. Mixing of Two Gases.

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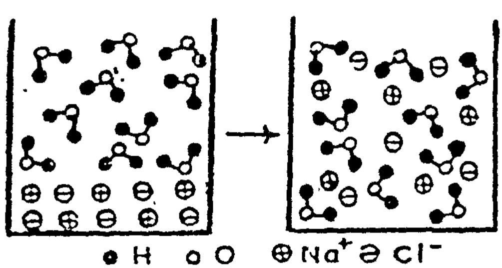

Fig. 4·2 Dissolution of NaCl in Water.

From these examples, it is clear that when spontaneous process occurs the system becomes more chaotic or in other words the degree of disorder or chaos or randomness increases. On the other hand, in spontaneous processes the entropy also increases. Thus, the **entropy** may be regarded *as a measure of degree of disorder or randomness.*

By definition it is clear that when heat is given to the system, the entropy of the system increases and hence the disorder or chaos also increases. Thus, when a solid is melted or a liquid is evaporated, the entropy of the system increases. This is illustrated in Fig. 4·3 A piece of copper is composed of Cu atoms arranged in regular manner when it is in solid state. The atoms have fixed positions

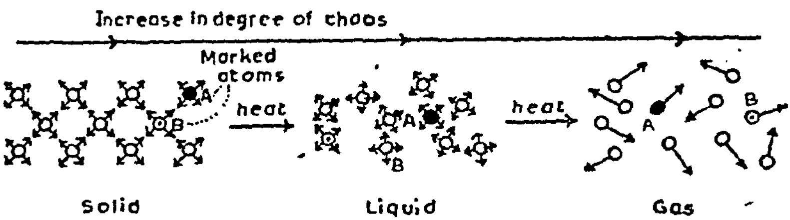

Fig. 4·3 Increase in Degree of chaos from Solid to Gaseous state.

and their vibrations are small. When heat is supplied to melt it, the atoms remain no longer fixed to a particular location as shown by marked atoms A and B and move from one place to another. Thus, chaos has increased. Continue heating the copper till it boils and converts into gaseous state. The atoms are now more free to move at random and the disorder has further increased. Since the randomness of a substance increases from solid to gaseous state, the entropy also increases in the same order. Thus, the entropy of a substance is higher in gaseous state and lower in solid state.

(ii) Entropy as a Function of Thermodynamic Probability.

The **thermodynamic probability** of a system is defined as *the maximum number of different ways in which a system in the given state may exist.* To understand the meaning of thermodynamic probability let us take four **indistinguishable** coins in a box and shake them. There are, in all, the following five possible states (complexions or microstates) in which the coins may be found arranged in the box.

(*i*) All the four coins showing heads.

(*ii*) Three coins showing heads and one showing tail.

(*iii*) Two coins showing heads and two showing tails.

(*iv*) One coin showing head and three showing tails.

(*v*) All the four coins showing tails.

On the other hand, if the coins are **distinguishable**, then the possible number of ways (microstates) or the probability of getting the above five states would be as given below. Here, H and T stand for head and tail showing respectively and subscripts 1, 2, 3, and 4 distinguish the four coins.

State		Arrangements	Total numbr of arrangements (microstates)
(*i*)	4 heads	$H_1H_2H_3H_4$	...1
(*ii*)	3 heads, 1 tail	$H_1H_2H_3T_4$, $H_1H_2T_3H_4$, $H_1T_2H_3H_4$, $T_1H_2H_3H_4$	...4
(*iii*)	2 heads, 2 tails	$H_1H_2T_3T_4$, $H_1T_2H_3T_4$, $H_1T_2T_3H_4$, $T_1H_2H_3T_4$, $T_1H_2T_3H_4$, $T_1T_2H_3H_4$	...6
(*iv*)	1 head, 3 tails	$T_1T_2T_3H_4$, $T_1T_2H_3T_4$, $T_1H_2T_3T_4$, $H_1T_2T_3T_4$	...4
(*v*)	4 tails.	$T_1T_2T_3T_4$	...1

The probability of getting 2 heads and 2 tails is highest and is six times as great as of getting either 4 heads or 4 tails. Now, if a large number of such boxes containing four distinguishable coins are shaken, the number of boxes showing 2 heads and 2 tails would be maximum because this state has large number of arrangements or higher probability.

We know that in a spontaneous process, the entropy increases and becomes maximum at equilibrium. Equilibrium position, as already stated, is a state of maximum disorder or chaos. The maximum disorder is attained when the molecules are distributed in maximum possible ways *i.e.*, when the thermodynamic probability becomes high. Thus, we see that the system moves from a less probable state to a more probable state. Entropy, on the other hand, also changes from a lower value to a higher value. Hence **entropy** *may be taken as the function of thermodynamic probability i.e.*,

$$S = f(W)$$

where W is the thermodynamic probability.

Consider two systems having entropies S_1 and S_2, and thermodynamic probabilities W_1 and W_2. Then

$$S_1 = f(W_1)$$
$$S_2 = f(W_2)$$

The two systems are now mixed and let the resulting entropy and the thermodynamic probability of the combined system be S and W respectively, then

$$S = f(W) \qquad ...(4\cdot33)$$

Since entropy is an additive property, the total entropy of the combined system is given by

$$S = S_1 + S_2 = f(W_1) + f(W_2) \qquad ...(4\cdot34)$$

The probability is a multiplicative factor hence the resulting thermodynamic probability of the combined system is given by

$$W = W_1 \times W_2 \qquad ...(4\cdot35)$$

Substituting for S from Eq. (4·34) and W from Eq. (4·35) in Eq. (4·33); we obtain

$$f(W_1) + f(W_2) = f(W_1 \times W_2) \qquad ...(4\cdot36)$$

This condition can be satisfied only when the function is logarithmic. Hence, it may be written that

$$S = k \ln W + C \qquad ...(4\cdot37)$$

where k and C are constants. The constant k is found to be Boltzmann constant. Further in case of a perfect crystal the entropy is zero at 0°K, (**third law**). The perfect crystal has only one arrangement at 0°K, hence the value of S can be zero only when the value of C is zero. Hence, the value of C is zero and Eq. (4·37) takes the form

$$S = k \ln W \qquad ...(4\cdot38)$$

This is called the **Plancks-Boltzmann equation** and gives a quantitative relationship between the entropy and the thermodynamic probability of a system.

Molecular Basis of Entropy

Thermodynamics deals with the properties of bulk matter or macroscopic states and the knowledge of structure of matter is not required. But our understanding of thermodynamic functions, such as entropy, can be enhanced if we express entropy in terms of molecular properties.

The thermodynamic state can be described in two ways : (*i*) **macroscopic description** and (*ii*) **microscopic description**, For example, consider a gaseous system in equilibrium. The macroscopic description of this system may be given by specifying the state properties, like P V, and T. On the other hand, the microscopic description involves a detailed analysis of the distribution of molecules in various energy levels corresponding to the different positions and velocities of all the molecules at any instant. Since molecules are moving at random with changing velocities, a particular microstate is valid only for an instant and changes rapidly. Since the

system is in equilibrium, the state properties do not change, hence the macrostate remains constant but the microstates are changing. This shows that for a particular macrostate there are a number of microstates associated with it.

These various microscopic states, depending on the number of available energy levels, are the number of ways in which a particular macrostate of system can be realized and hence is a measure of probability. As we know that the probability is the measure of entropy of the system, the greater the number of available energy levels, the greater is the number of microstates or probability and consequently the entropy will be higher With this molecular interpretation of entropy, we can explain the entropy behaviour in a number of phenomena.

When a gas expands spontaneously into a vacuum, the entropy of the system increases. It can be explained on the fact that in the process of expansion the volume of the gas increases and consequently the number of positions, in space, available to a molecule increases. This results in the increase in the number of microstates and hence increase in the probability. Since the probablity increases, the expansion is associated with the increase in entropy.

When heat is given to the system to raise its temperature, the energy of the system increases and a few more energy levels become available to the molecules. This leads to the increase in the number of microstates and hence the entropy increases.

The entropy depends on the molecular complexity of a substance. Atoms are spherically symmetrical hence their orientation contributes nothing to the disorder of the system. On the other hand; diatomic and polyatomic molecules are associated with rotational and vibrational energies. Since these energies are quantized, there is a larger number of possible energy levels for these molecules and hence the entropy is high.

The symmetry of a molecule also affects its entropy. The molecules with symmetry have smaller entropy because they are [illegible] comparatively ordered form. Cyclic molecules, being more sy[illegible]trical, have lower entropy than those of the corresponding non[illegible] isomers.

The entropy of a *mixture of two* gases is higher than [illegible] of the entropies of individual gases under similar c[illegible] temperature and pressure. The difference of these two [illegible] known as **entropy of mixing**. The increase in [illegible] explained on the fact that the disorder increases [illegible] hence the entropy increases.

WORK AND FREE ENERGY FUNCTIONS

Need of the New Functions

As already discussed that all the natural or spontaneous processes proceed towards the condition of maximum stability *i.e.*, equilibrium. In an isolated system, a spontaneous change is accompanied by an increase in entropy and hence at equilibrium the entropy becomes maximum. In an isolated system the internal energy remains constant. Thus, we can say that *in a system of constant energy, the equilibrium position is that of maximum entropy.* On the other hand, in mechanical systems a spontaneous process is accompained with a decrease in potential energy of the system and at equilibrium the energy of the system becomes minimum. In chemical systems, however, this statement is inadequate because some endothermic reactions are also spontaneous. In endothermic reactions, the heat is absorbed and thus the energy of the system increases. However, for the chemical system we can state more safely that *in a system of constant entropy the equilibrium position is that of minimum energy.*

In most chemical processes neither the entropy nor the energy is held constant and both change simultaneously during the process. Further, for some reactions both these factors are favourable and in other reactions one is favourable and the other is not. For example, in the following spontaneous process at 25°C,

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$$

the heat of reaction $\triangle H°$ is -68320 cal mole^{-1} and the entropy change is $-39{\cdot}0$ cal deg^{-1}. In this reaction the energy change is favourable because it is decreasing but the entropy change is unfavourable because it is also decreasing. Take another example of vaporization of benzene;

$$C_6H_6(l) = C_6H_6(g)$$

which is a spontaneous process. For this process the enthalpy change and the entropy change are $+8100$ cal mole^{-1} and $+23{\cdot}04$ cal deg^{-1} respectively. In this case, the energy change is unfavourable because heat is absorbed but the entropy change is favourable because it is increasing.

These examples clearly show that neither energy change nor entropy change alone can determine the direction of spontaneous change. Now what is needed is to relate these two factors in some way so that they act together to drive the system to equilibrium. To do so, two thermodynamic functions, called **Helmholtz free energy** or **work function**, *A* and **Gibbs free energy** *G* (also denoted by *F*) have been introduced.

Definition of the Two Functions

These two functions are defined by the following relations :

$$A = E - TS \quad ...(4\cdot39)$$
$$G = H - TS \quad ...(4\cdot40)$$

where E, H, S, and T are as usual, the internal energy, enthalpy, entropy and temperature of the system respectively. Since E, H, S and T are thermodynamic functions, A and G are also thermodynamic functions. Since changes in E, H, and S can only be measured and dealt with, so is the case with A and G. We can only measure and deal with $\triangle A$ and $\triangle G$ and not A and G. Equations (4·39) and (4·40) may be modified depending on the conditions of the change.

Suppose a system undergoes a thermodynamic change from state 1 to state 2. Let the work function, internal energy, entropy, and temperature in state 1 be represented by A_1, E_1, S_1 and T_1 respectively and in state 2 by A_2, E_2, S_2, and T_2 respectively. From Eq. (4·39), we can write

$$A_1 = E_1 - T_1S_1 \quad ...(4\cdot41)$$
$$A_2 = E_2 - T_2S_2 \quad ...(4\cdot42)$$

Subtracting Eq. (4·41) from Eq. (4·42), we get

$$A_2 - A_1 = (E_2 - E_1) - (T_2S_2 - T_1S_1)$$
$$\text{or} \quad \triangle A = \triangle E - \triangle(TS) \quad ...(4\cdot43)$$

In an isothermal process where $T_2 = T_1 = T$, Eq. (4·43) can be written as

$$\triangle A = \triangle E - T\triangle S \quad ...(4\cdot44)$$

Exactly in the same manner Eq. (4·40) can lead to

$$\triangle G = \triangle H - T\triangle S \quad ...(4\cdot45)$$

Relation between $\triangle G$ and $\triangle A$

Subtracting Eq. (4·44) from (4·45), we get

$$\triangle G - \triangle A = \triangle H - \triangle E \quad ...(4\cdot46)$$

we know that at constant pressure

$$\triangle H = \triangle E + P\triangle V \quad ...(4\cdot47)$$

substituting the value of $\triangle H$ from Eq. (4·47) in Eq. (4·46). we get

$$\triangle G - \triangle A = \triangle E + P\triangle V - \triangle E$$
$$\text{or} \quad \triangle G = \triangle A + P\triangle V \quad ...(4\cdot48)$$

This relation is true only to processes occurring at constant temperature and constant pressure.

In case of solids and liquids where the volume change $\triangle V$ is negligibly small, $P\triangle V$ is taken as negligible in Eq. (4·48), then

$$\triangle G \simeq \triangle A \quad ...(4\cdot49)$$

Most of the chemical processes are carried out at constant atmospheric pressure and the heat of reaction ΔH is usually measured Hence, Gibbs free energy ΔG is mostly used. **Gibbs free energy** is commonly known as **free energy.**. Now we shall restrict our discussions to free energy only. However, similar arguements are applicable to ΔA also.

Example 10. *For a chemical reaction the value of ΔH and ΔS are —17·90 kcal and -44 50 cal deg^{-1} respectively. These values do not change much by temperature changes. Calculate the value of ΔG of the reaction at (a) 300°K and (b) 1000°K*

Solution. We know that

$$\Delta G = \Delta H - T\Delta S$$

(*a*) In this case

$$\Delta H = -17{\cdot}90 \text{ kcal} = -17900 \text{ cal}$$

$$\Delta S = -44{\cdot}50 \text{ cal deg}^{-1}$$

and $T = 300°\text{K}$

$$\therefore \quad \Delta G = -17900 - 300 \times (-44{\cdot}50)$$
$$= -17900 + 13350$$
$$= -4550 \text{ cal}$$

(*b*) In this case T = 1000°K

$$\therefore \quad \Delta G = -17900 - 1000 \times (-44{\cdot}50)$$
$$= -17900 + 44500$$
$$= +26600 \text{ cal.}$$

Physical significance of Free Energy

(*i*) **ΔG as a measure of the tendency of a spontaneous process to take place**

Examination of the relation

$$\Delta G = \underset{\text{Energy term}}{\Delta H} - \underset{\text{Entropy term}}{T\Delta S}$$

shows that free energy change is made up of two terms : an energy term and an entropy term. We know that in a system of constant entropy the spontaneous change is accompanied by decrease in energy and in a system of constant energy, the spontaneous change is accompanied by increase in entropy. In a given process, if both these changes occur simultaneously, *i.e.*, when ΔH is negative and ΔS is positive, it can be safely assumed that the spontaneous change would occur. When ΔH is negative and ΔS is positive and since T is always positive, it is evident from the above equation that ΔG will be negative. It can, therefore, be concluded that for a spontaneous change ΔG is negative.

Free energy as a balance between the energy and entropy terms is illustrated in Fig. 4·4. The position of the suspended rod depends

on the magnitude and the direction of the forces acting upon it. This can be compared with the free energy change, the sign and magnitude of which depend on the energy and entropy terms. Fig. (*a*) shows the position of equilibrium when $\Delta H = T\Delta S$ *i.e.*, $\Delta G = 0$.

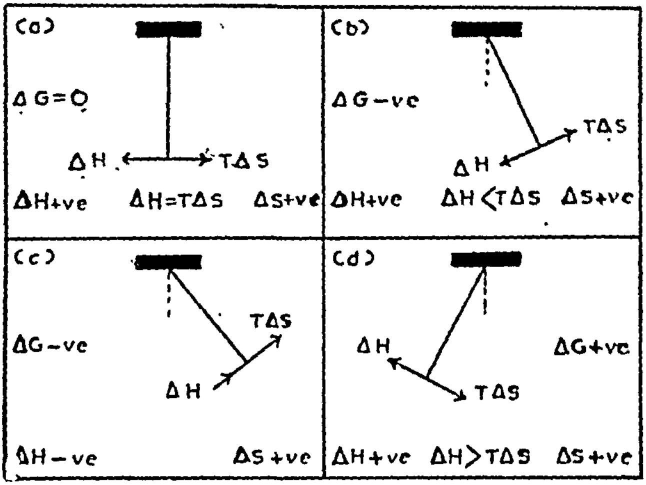

Fig. 4·4 Pictorial Representation of Free Energy as a Balance between Energy and Entropy

Fig. (*b*) and Fig. (*c*) show that ΔG is negative and equilibrium is disturbed towards right. Fig. (*d*) shows that ΔG is positive and the equilibrium is disturbed towards left. The swing towards right (when ΔG is negative) shows the spontaneous process to occur in the forward direction and the swing towards left (when ΔG is positive) shows the spontaneous process to occur in the opposite direction.

Thus, we see that ΔG may be taken as a measure of the tendency of a spontaneous process to occur. To summarize,

When $\Delta G < 0$ *i.e.*, negative,	the process tends to occur spontaneously
$\Delta G = 0$	the system is at equilibrium
$\Delta G > 0$ *i.e.*, positive,	the process tends to occur spontaneously but in opposite direction.

Example 11. *Calculate the free energy change of the following reaction at 25°C*

$$SO_2(g) + \tfrac{1}{2}O_2(g) = SO_3(g)$$

For this reaction the enthalpy change and entropy given as −23490 cal and −22·7 cal deg⁻¹ respectively.

Is this reaction thermodynamically possible?

Solution. We know that

$$\Delta G = \Delta H - T\Delta S$$

Here $\Delta H = -23490$ cal mole^{-1}

$\Delta S = -22\cdot7$ cal deg^{-1}

T = 273+25 = 298°K

$\therefore \Delta G = -23490 - 298\,(-22\cdot7)$

$= -16726$ cal.

Since the free energy change is negative the reaction is thermodynamically possible at 25°C.

(ii) ΔG as a measure of the useful work of a process

By definition

$$G = H - TS$$

we know that $H = E + PV$

$$\therefore \quad G = E + PV - TS \qquad ...(4\cdot50)$$

Differentiating both the sides of Eq. (4·50), we get

$$dG = dE + PdV + VdP - TdS - SdT \qquad ...(4\cdot51)$$

For a process occurring at constant temperature and constant pressure $i.e.$, where $dT=0$ and $dP=0$, Eq. (4·51) reduces to

$$dG = dE + PdV - TdS \qquad ...(4\cdot52)$$

For a reversible process, from the definition of entropy

$$TdS = dq_{rev}$$

Substituting in Eq. (4·52), we get

$$dG = dE + PdV - dq_{rev} \qquad ...(4\cdot53)$$

From the first law of thermodynamics

$$dE = dq_{rev} - dw_{max}$$

Substituting for dE in Eq. (4·53), we get

$$dG = dq_{rev} - dw_{max} + PdV - dq_{rev}$$

or $$-dG = dw_{max} - PdV \qquad ...(4\cdot54)$$

PdV represents the work associated with the volume change of the system against a constant pressure P which is wasted. dw_{max} is the maximum work done by the system. Hence, $dw_{max} - PdV$ gives the **useful** or **net work** :

$$dw_{max} - PdV = dw_{useful}$$

$$\therefore \quad -dG = dw_{useful} \qquad ...(4\cdot55)$$

Thus, decrease in free energy of the system is a measure of the net useful work obtainable from it at constant temperature and pressure. An example of useful work is the electric work done in a galvanic cell.

Dependence of Free energy on Pressure and Temperature

By definition

$$G = H - TS$$

Since $H = E+PV$

$\therefore \quad G = E+PV-TS$

For a general change

$$dG = dE+PdV+VdP-TdS-SdT \quad \text{...(4·56)}$$

From the first law of thermodynamics,

$$dE = dq-dw \quad \text{...(4·57)}$$

It is assumed that the process is reversible and no work other than that of volume change is occurring, hence

$$dq = TdS$$

and

$$dw = PdV$$

Substituting in Eq. (4·57), we get

$$dE = TdS-PdV \quad \text{...(4·58)}$$

Combining Eq. (4·56) and Eq. (4·58), we get

$$dG = VdP-SdT \quad \text{...(4·59)}$$

This equation takes different forms under different conditions:

(*i*) **At constant temperature** : *i.e.*, when $dT = 0$. Eq. (4·59) takes the form

$$dG = VdP$$

or

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{...(4·60)}$$

(*ii*) **At constant pressure** *i.e.*, when $dP = 0$., Eq. (4·59) takes the form

$$dG = -SdT$$

or

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{...(4·61)}$$

Free Energy change with Pressure For an Ideal Gas

At constant temperature, it follows that

$$dG = VdP \quad \text{...(4·62)}$$

If the pressure changes from P_1 to P_2, the corresponding free energy will change from G_1 to G_2. Integrating Eq. (4·62) between these limits, we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP \quad \text{...(4·63)}$$

For an ideal gas,

$$V = \frac{nRT}{P}$$

Solution. We know that

$$\Delta G = \Delta H - T\Delta S$$

Here $\Delta H = -23490$ cal mole^{-1}

$\Delta S = -22{\cdot}7$ cal deg^{-1}

$T = 273+25 = 298°K$

$$\therefore \quad \Delta G = -23490-298\,(-22{\cdot}7)$$
$$= -16726 \text{ cal.}$$

Since the free energy change is negative the reaction is thermodynamically possible at 25°C.

(*ii*) ΔG as a measure of the useful work of a process

By definition

$$G = H - TS$$

we know that $H = E + PV$

$$\therefore \quad G = E + PV - TS \qquad ...(4{\cdot}50)$$

Differentiating both the sides of Eq. (4·50), we get

$$dG = dE + PdV + VdP - TdS - SdT \qquad ...(4{\cdot}51)$$

For a process occurring at constant temperature and constant pressure *i.e.*, where $dT=0$ and $dP=0$, Eq. (4·51) reduces to

$$dG = dE + PdV - TdS \qquad ...(4{\cdot}52)$$

For a reversible process, from the definition of entropy

$$TdS = dq_{rev}$$

Substituting in Eq. (4·52), we get

$$dG = dE + PdV - dq_{rev} \qquad ...(4{\cdot}53)$$

From the first law of thermodynamics

$$dE = dq_{rev} - dw_{max}$$

Substituting for dE in Eq. (4·53), we get

$$dG = dq_{rev} - dw_{max} + PdV - dq_{rev}$$

or $$-dG = dw_{max} - PdV \qquad ...(4{\cdot}54)$$

PdV represents the work associated with the volume change of the system against a constant pressure P which is wasted. dw_{max} is the maximum work done by the system. Hence, $dw_{max}-PdV$ gives the **useful** or **net work** :

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Dependence of Free energy on Pressure and Temperature

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For a general change

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From the first law of thermodynamics,

$$dE = dq-dw \qquad ...(4{\cdot}57)$$

It is assumed that the process is reversible and no work other than that of volume change is occurring, hence

$$dq = TdS$$

and $\quad dw = PdV$

Substituting in Eq. (4·57), we get

$$dE = TdS-PdV \qquad ...(4{\cdot}58)$$

Combining Eq. (4·56) and Eq. (4·58), we get

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This equation takes different forms under different conditions:

(*i*) **At constant temperature** : *i.e.*, when $dT = 0$. Eq. (4·59) takes the form

$$dG = VdP$$

or $$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad ...(4{\cdot}60)$$

(*ii*) **At constant pressure** *i.e.*, when $dP = 0$., Eq. (4·59) takes the form

$$dG = -SdT$$

or $$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad ...(4{\cdot}61)$$

Free Energy change with Pressure For an Ideal Gas

At constant temperature, it follows that

$$dG = VdP \qquad ...(4{\cdot}62)$$

If the pressure changes from P_1 to P_2, the corresponding free energy will change from G_1 to G_2. Integrating Eq. (4·62) between these limits, we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP \qquad ...(4{\cdot}63)$$

For an ideal gas,

$$V = \frac{nRT}{P}$$

Substituting for V in Eq. (4·63), we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\text{or } \Delta G = G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\text{or } \Delta G = 2{\cdot}303\ nRT \log_{10} \frac{P_2}{P_1} \qquad \ldots(4{\cdot}64)$$

Since G is state function, Eq. (4·64) gives free energy changes whether the process is carried out reversibly or irreversibly.

Example 12— *Calculate the free energy change when 4 moles of an ideal gas expands from a pressure of 10 atm to 1 atm at 25°C.*

Solution. We know that

$$\Delta G = 2{\cdot}303\ nRT \log_{10} \cancel{\frac{P_1}{P_2}}\ \frac{P_2}{P_1}$$

Here $n = 4$ moles

$R = 1{\cdot}987$ cal deg^{-1} mole^{-1}

$T = 273+25 = 298$°K

$P_1 = 10$ atm

$P_2 = 1$ atm.

$$\therefore \Delta G = 2{\cdot}303 \times 4 \times 1{\cdot}987 \times 298 \times \log_{10} 1/10$$
$$= -5440 \text{ cal}$$

The Gibbs-Helmholtz Equation

At constant pressure, the change of free energy with temperature is given by

$$\left(\frac{\partial G}{\partial T}\right)_P = -S. \qquad \ldots(4{\cdot}65)$$

Suppose a system changes reversibly and isothermally from state 1 to state 2. If free energy and entropy of the system in state 1 are G_1 and S_1 respectively and in state 2, G_2 and S_2 respectively, then the entropy change of the system is given by

$$\Delta S = S_2 - S_1 \qquad \ldots(4{\cdot}66)$$

From Eq. (4·65), we can write

$$S_1 = -\left(\frac{\partial G_1}{\partial T}\right)_P \text{ and } S_2 = -\left(\frac{\partial G_2}{\partial T}\right)_P$$

Substituting these values of S_1 and S_2 in Eq. (4·66), we get

$$\Delta S = -\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right]$$

or $$= -\left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_P$$

or $$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad ...(4\cdot67)$$

For an isothermal process

$$\Delta G = \Delta H - T\Delta S$$

Substituting the value of ΔS in this equation from Eq. (4·67), we get

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad ...(4\cdot68)$$

This equation was derived independently by J.W. Gibbs and H. Von Helmholtz and is known as **Gibbs-Helmholtz equation.**

A corresponding derivation employing the work function A and internal energy E for an isothermal reversible processe at constant volume yields another form of Gibbs-Helmholtz equation :

$$\Delta A = \Delta E + T\left(\frac{\partial \Delta A}{\partial T}\right)_V \qquad (4\cdot69)$$

Importance of Gibbs-Helmholtz Equations

Gibbs-Helmholtz equations are applicable to any physical process. Some important uses are given below :

(*i*) Eqs (4·68) and (4·69), though derived for reversible processes are applicable for irreversible process also because they involve ΔG, ΔH, ΔA and ΔE which do not depend on the path of the process.

(*ii*) They help to calculate the values of ΔH or ΔE provided ΔG or ΔA and their respective temperature coefficients are known.

Example 13. *For the following reaction.*

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

the free energy changes at 25°C and 35°C are —3·98 and —3·37 kcal. Calculate the heat of reaction at 35°C.

Solution. We know that

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

Also $$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{(G_2 G_1)}{T_2 - T_1}$$

Here $G_1 = -3\cdot98$ kcal

$G_2 = -3\cdot37$ kcal

$$T_1 = 273+25 = 298°K$$
$$T_2 = 273+35 = 308°K$$
$$\therefore \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-3{\cdot}37-(-3{\cdot}98)}{308-298} = \frac{0{\cdot}61}{10}$$
$$= 0{\cdot}061$$

At 35°C,

$$\Delta G = -3{\cdot}37 \text{ kcal}$$
$$T = 308°K$$
$$\therefore \quad -3{\cdot}37 = \Delta H + 308\ (0{\cdot}061)$$
$$\therefore \quad \Delta H = -3{\cdot}37 - 18{\cdot}79 = -22{\cdot}16 \text{ kcal}$$

(*iii*) If ΔG of a process is known at a given temperature then its value at another temperature can be calculated provided that the difference of temperature is so small that the rate of change of free energy with temperature remains practically constant over this temperature range.

Example 14. *For the following reaction.*

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l)$$

the values of enthalpy change and free energy change are —68·32 and —56·69 kcal respectively at 25°C. Calculate the value of free energy change at 30°C.

Solution. We know that

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

Here $\Delta G = -56{\cdot}69$ kcal

$\Delta H = -68{\cdot}32$ kcal

$T = 273 + 25 = 298°K$

$$\therefore \quad -56{\cdot}69 = -68{\cdot}32 + 298\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\text{or} \quad \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-56{\cdot}69 + 68{\cdot}32}{298} = 0{\cdot}039$$

Assuming that $\left(\frac{\partial \Delta G}{\partial T}\right)_P$ remains constant over this range of temperature, at 30°C we can write

$$\Delta G = -68{\cdot}32 + 303 \times 0{\cdot}039$$
$$= -68{\cdot}32 + 11{\cdot}81$$
$$= -56{\cdot}51 \text{ kcal.}$$

(*iv*) With the help of Gibbs-Helmholtz equation the heat change of the reaction can be calculated from the emf of the Galvanic cell

Suppose n faradays or $n\mathcal{F}$ coulombs of electricity is yielded by a cell reversibly at constant temperature and pressure. If $\mathcal{E}$ is the

emf of the cell, then the electrical work done will be $n\mathcal{F}\mathcal{E}$. Under reversible conditions, this work done will be maximum and equal to the decrease in free energy, *i.e.*,

$$-\triangle G = n\mathcal{F}\,\mathcal{E}$$

Substituting for $\triangle G$ in Eq. (4·68), we get

$$-n\mathcal{F}\mathcal{E} = \triangle H - T\left[\frac{\partial(n\mathcal{F}\mathcal{E})}{\partial T}\right]_P$$

$$-n\mathcal{F}\mathcal{E} = \triangle H - n\mathcal{F}T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$$

$$\text{or} \quad \mathcal{E} = -\frac{\triangle H}{n\mathcal{F}} + T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P \qquad (4{\cdot}70)$$

Thus, if we know the value of $\mathcal{E}$ and its temperature coefficients $\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$ the value of heat change $\triangle H$ of a reaction occurring in the cell can be calculated. The details are given in chapter 7.

Besides these applications, Gibbs-Helmholtz equations are useful in many ways which are beyond the scope of this book.

TEST YOUR KNOWLEDGE

1. Complete the following :

(*i*) $\ldots\ldots = \frac{dq_{rev}}{T}$.

(*ii*) $\triangle S = n\ldots\ln\frac{T_2}{T_1} + n\ldots\ln\frac{V_2}{V_1}$

(*iii*) $\triangle S = nC_P \ln\frac{T_2}{T_1} + nR\ln\ldots$

(*iv*) $\triangle S_{system} > \frac{q_{irrev}}{\ldots\ldots}$

(*v*) $S = \ldots\ln W$

(*vi*) $\triangle F = \ldots - T\triangle S$

(*vii*) $\triangle A = \ldots - T\triangle S$

(*viii*) $-dG = \ldots - PdV$

(*ix*) $dG = dP - S\ldots$

(*x*) $\left(\frac{\partial G}{\partial P}\right)_T = ..V$

(*xi*) $\left(\frac{\partial G}{\ldots}\right) = -S$

(*xii*) $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

(*xiii*) $\Delta A = \Delta E + T\left(\frac{\partial \Delta A}{\partial T}\right)_V$

(*xiv*) $\mathcal{E} = -\frac{\Delta H}{n\mathcal{F}} + T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$

2. Give a term for each of the following :

(*i*) Processes occurring without the assistance of any external energy.

(*ii*) The fraction of heat absorbed converted into work by a heat engine.

(*iii*) The amount of heat absorbed reversibly by a system divided by the absolute temperature at which it is absorbed.

(*iv*) Maximum number of different ways in which a system in a given state may exist.

(*v*) Measure of useful work obtainable from a system.

3. Fill in the blanks with appropriate words :

(*i*) Spontaneous processes are.........and can be reversed only when work is done......the system.

(*ii*) All natural or spontaneous processes tend to proceed to a state of ....

(*iii*) Heat can flow from a body at......temperature to a body at........ temperature.

(*iv*) dq is an......differential but dq/T is an......differential.

(*v*) In a reversible process, the entropy change of the universe is......

(*vi*) ......is a measure of degree of disorder or chaos.

(*vii*) The entropy of a substance in the liquid state is higher than its entropy in......state and lower than that in......state.

(*viii*) Equilibrium position is a state of......disorder or chaos.

(*ix*) More the number of microstates associated with a macrostate,...... is the probability.

(*x*) Entropy is a......of thermodynamic probability.

(*xi*) In a system of constant entropy, the equilibrium position is that of......energy.

(*xii*) In a system of constant energy, the equilibrium position is that of......entropy.

(*xiii*) At equilibrium the change in free energy is......

(*xiv*) In a spontaneous process, the free energy......

(*xv*) ......is a measure of useful work.

KEY

1. (*i*) dS. (*ii*) C_v, R. (*iii*) P_1/P_2. (*iv*) T. (*v*) k. (*vi*) ΔH. (*vii*) ΔE. (*viii*) dw_{max}. (*ix*) V, dT. (*x*) V, (*xi*) $-S$, (*xii*) ΔG, (*xiii*) ΔA (*xiv*) ΔH.

2. (*i*) Spontaneous processes, (*ii*) Efficiency of heat engine, (*iii*) Entropy change of the system, (*iv*) Thermodynamic probability, (*v*) Free energy.

3. (*i*) irreversible, on, (*ii*) equilibrium, (*iii*) higher, lower, (*iv*) inexact, exact, (*v*) constant, (*vi*) Entropy, (*vii*) solid, gaseous, (*viii*) maximum, (*ix*) more, (*x*) function, (*xi*) minimum, (*xii*) maximum, (*xiii*) zero, (*xiv*) decreases, (*xv*) Free energy.

QUESTIONS

1. Write notes on :
   (*i*) Spontaneous processes.
   (*ii*) Irreversible and reversible processes.
   (*iii*) Second law of thermodynamics.
   (*iv*) Entropy.
   (*v*) *Physical significance of entropy.*
   (*vi*) Free energy and its Physical significance.
2. Give the various statements of the second law of thermodynamics and show that all of them lead to the same goal.
3. State second law of thermodynamics and explain the conditions under which heat can be converted into work.
4. Derive the concept of entropy from the second law of thermodynamics.
5. Give the concept of entropy and its relation to the concept of randomnese or chaos.
6. How entropy is related to thermodynamic probability ? Derive the expression $S = k \ln W$.
7. Define entropy and give its physical significance.
8. Discuss the entropy change in
   (*i*) reversible processes, and
   (*ii*) irreversible processes.
9. *State the second law of thermodynamics in terms of entropy* change. Show that the entropy is a state function.
10. Derive expressions for the entropy changes for n moles of an ideal gas in
    (*i*) isothermal process,
    (*ii*) isobaric process, and
    (*iii*) isochoric process.
11. Write a note on molecular basis of entropy.
12. Define the following terms :
    (*i*) Gibbs free energy.
    (*ii*) Helmholtz free energy or work function
    What is the need of these functions ? Deduce the relationship between the two. Under what conditions $\Delta G = \Delta A$?

13. Discuss

(*i*) ΔG as a measure of useful work of a process.

(*ii*) ΔG as a measure of tendency of a spontaneous process to occur.

14. Obtain expressions showing the dependence of free energy on pressure and temperature.

15. Derive Gibbs-Helmholtz equation and discuss its applications.

16. Calculate the entropy change when 2 moles of an ideal gas (Cp = 7 cal deg^{-1} mole^{-1}) as it changes from 300° K and 0·5 atm to 1000°K and 5 atm.

[Ans. 7·708 cal deg^{-1}]

17. Calculate the entropy change when 14 gm of nitrogen are allowed to expand from a volume of 2 lit to a volume of 20 lit at 27°C.

[Ans. 2·289 cal deg^{-1}]

18. Calculate the entropy change when 16 gm of helium (Cp = 5 cal deg^{-1} mole^{-1}) are heated from 20°C to 90°C (*i*) at constant volume and (*ii*) at constant pressure.

[Ans. (*i*) 4·285 cal deg^{-1}, (*ii*) 2·581 cal deg^{-1}]

19. Calculate the entropy change involved in expanding 5 moles of an ideal gas from 30 lit at 4 atm pressure to 100 lit at 2 atm pressure. (Cp = 7·4 cal deg^{-1} mole^{-1}).

[Ans. 25·789 cal deg^{-1}]

20. Calculate the entropy change when one mole of an ideal gas (Cv = 5·41 cal deg^{-1} mole^{-1}) is expanded from a volume of 50 lit at 50°C to a volume of 100 lit at 200°C.

[Ans. 3 442 cal deg^{-1}]

21. Calculate the entropy change experienced by 4 moles of an ideal gas (Cp = 9·88 cal deg^{-1} mole^{-1}) when heated from 100°C at 1 atm pressure to 400°C at 2 atm pressure.

[Ans. 17·819 cal deg^{-1}]

22. Calculate the entropy change when 20 gm of aluminium is heated from 50°C to 100°C. The sp. heat of Al over this temperature range is 0·168 cal gm^{-1}.

[Ans. 0·4842 cal deg^{-1}]

23. Calculate the entropy change when 24 gm. of ice is converted into water at 0°C. The molar heat of fusion of ice is 1440 cal mole^{-1}.

[Ans. 7·033 cal deg^{-1}]

24. Calculate the entropy change when 20 gm of water at 0°C is heated to 100°C. The specific heat of water is equal to 1.

[Ans. 6·24 cal deg^{-1}]

25. Calculate the entropy change when 2 moles of water supercooled to —10°C freezes isothermally. The molar heat of fusion of ice at 0°C is 1440 cal mole^{-1} and the molar heat capacities of ice and water are 9·0 and 18·0 cal deg^{-1} mole^{-1}.

[Ans. —9·8762 cal deg^{-1}]

26. For a certain reaction at 25°C, the values of ΔH and ΔS are —67650 cal and —20·7 cal deg^{-1} respectively; calculate ΔG of the process at 25°C.

[Ans. —61481 cal]

27. Calculate the free energy change of the following reaction at 25°C.

$$H_2(g)+I_2(s) = 2HI(g)$$

For this reaction the enthalpy change is 12400 cal and the entropy change is 39·71 cal deg^{-1}. Is this reaction thermodynamically possible at this temperature?

[Ans. +570 cal; No]

28. Calculate the free energy change when 2 moles of an ideal gas expands from a pressure of 25 atm to 2·5 atm at 25°C.

[Ans. —2727 cal]

29. For the reaction

$$CO\ (g) + \tfrac{1}{2}O_2\ (g) = CO_2\ (g)$$

the free energy changes at 25°C and 35°C are —61·45 and —61·24 kcal respectively. Calculate the heat of reaction at 25°C.

[Ans. — 67·63 kcal]

30. For the reaction

$$C\ (s) + O_2\ (g) = CO_2\ (g)$$

the values of enthalpy change and free energy change are —94·05 and —94·26 k cal respectively at 25°C. Calculate the value of free energy change at 35°C.

[Ans. —94·07 kcal]

5

Electrolytic Conductance

Introduction

Electrical energy may be transferred by the flow of electric charge from one point to another through matter in the form of electric current. Substances like copper, silver, mercury, platinum aqueous solutions of acids, bases and salts which allow the current to pass through them are called **conductors** of electricity. On the other hand, substances like mica, glass, wax, ebonite, etc., which do not allow the current to pass through are called **non-conductors** or **insulators.**

There are two requirements for the electric current to flow through substances; (*i*) presence of charge carriers in matter and (*ii*) force to move the charge carriers. Depending on the nature of charge carriers, the conductors may be divided broadly into two categories : (*i*) Electronic conductors and (*ii*) Ionic conductors. *Substances in which the charge-carriers are* **electrons** *are called* **electronic conductors**. For example, metals, alloys, graphite, etc., are electronic conductors. *Substances in which the charge carriers are ions, are called* **ionic conductors.** They are also called **electrolytic conductors** or **electrolytes.** For example, solutions of acids, bases and salts, the salts in molten state, etc., are electrolytes. There are many substances, the solution of which do not conduct electricity, are called **non-electrolytes.** In some substances like used cuprous sulphide, solution of metallic sodium in liquid ammonia, etc., the conduction of current is partly electronic and partly ionic. Such substances are known as **mixed conductors.** The electric force which is responsible for the movement of charge carriers is generally supplied by a battery or any other similar source of electric energy.

It is important to note that in electronic conductors the flow of current is not accompanied by any chemical change in it, while in ionic conductors or electrolytes, it causes chemical change. *The process of electrolyte conduction accompanying a chemical change in the electrolyte is known as* **electrolysis.** In this chapter we shall deal with the conductance of electricity in electrolytes only.

Mechanism of Electrolysis

To understand the mechanism of electrolysis, let us take an

example of electrolysis of molten NaCl. The electrolytic cell is shown in Fig. 5·1. It consists of two platinum electrodes immersed in molten NaCl and connected to a battery. The electrode which is

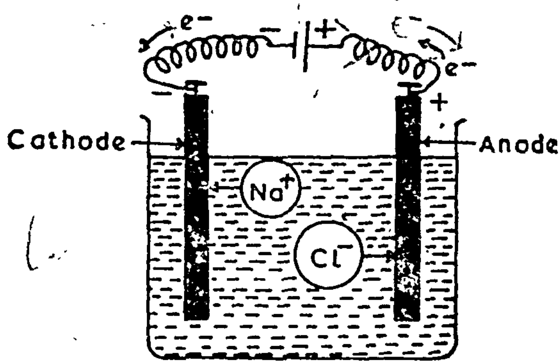


Fig. 5·1. Electrolysis of Molten Sodium Chloride

connected to the negative terminal of battery is called **cathode** and the other one connected to the positive terminal is called **anode.**

When current is passed through the electrolyte, it is seen that sodium is deposited at the cathode and chlorine gas is liberated at the anode. The phenomenon of electrolysis can be explained as follows. The molten sodium chloride consists of Na^+ ions and Cl^- ions. Na^+ ions being positive move towards cathode while Cl^- ions being negative move towards anode as shown in the figure. When a Na^+ ion touches the cathode, it takes up an electron from the cathode and gets reduced to sodium atom. This **cathode reaction** can be shown by the following equation :

$$Na^+ + e^- \rightarrow Na \qquad ...(5{\cdot}1)$$

Thus, sodium is deposited on the cathode. When a Cl^- ion touches the anode, it gives up an electron to the anode and gets oxidised to Cl atom. The **anode reaction** can be given by the following equation :

$$Cl^- \rightarrow Cl + e^- \qquad ...(5{\cdot}2)$$

Two chlorine atoms combine to form Cl_2 molecule.

$$2Cl \rightarrow Cl_2 \qquad ...(5{\cdot}3)$$

Thus, chlorine gas is liberated at the anode.

If an aqueous solution of sodium chloride is submitted to electrolysis, the mechanism of conduction of electricity is the same. *i.e.*, Na^+ ions move towards cathode and Cl^- ions move towards anode but a different chemical change occurs at the cathode. Instead of deposition of sodium, H_2 gas is evolved and NaOH is accumulated around the cathode. This phenomenon can be explained in the following way. The electrolytic solution contains Na^+ ions, Cl^- ions and traces of H^+ and OH^- ions from the slight dissociation of H_2O. The following reactions may occur at the cathode—

(i) $Na^{+}+e^{-} \rightarrow Na$

(ii) $H_2O \rightleftharpoons H^{+}+OH^{-}$

$$\frac{H^{+}+e^{-} \rightarrow \frac{1}{2}H_2}{H_2O+e^{-} \rightarrow OH^{-}+\frac{1}{2}H_2}$$

on combining

Reaction (*i*) is not possible because Na^+ ion is less readily discharged than H^+ ion from water. Thus, reaction (*ii*) represents the cathode reaction. It also explains the observed accumulation of NaOH round the cathode because Na^+ ions travel towards cathode and accumulate where OH^- ions are also being produced by the cathode reaction.

Faraday's Laws of Electrolysis. Micheal Faraday in 1834 established the laws of electrolysis after performing a number of experiments. These laws bear his name and deal with the quantitative chemical change of electrolytes during electrolysis. The laws are as follows:

First Law. *The mass of a substance produced at cathode or anode in electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.*

Second Law. *When the same quantity of electricity is passed through different electrolytes, the masses of different substances deposited or dissolved at the electrodes are directly proportional to their gram equivalent weights.*

Both these laws in the combined form may be stated as follows:

The number of gram equivalent weight of any substance produced or dissolved at electrodes is directly proportional to the quantity of electricity passed through the electrolyte.

Thus, if m gm of a substance of equivalent weight E is produced or dissolved by passing I amp of current for t sec, then m/E is the number of gram equivalent of the substance produced or dissolved and $I \times t$ is the quantity of electricity in coulombs passed.

Hence,
$$\frac{m}{E} \propto I \times t$$

$$= \frac{I \times t}{\mathcal{F}}$$

or
$$m = \frac{I \times t \times E}{\mathcal{F}} \qquad ...(5\cdot4)$$

where $1/\mathcal{F}$ is the proportionality constant and $\mathcal{F}$ is called **faraday.** If $\mathcal{F}$ is taken equal to $I \times t$ coulombs, Eq. (5 4) reduces to

$$m = E$$

i.e., the amount of substance produced or evolved is equal to its gram equivalent weight. Thus, **faraday** may be defined as *the quantity of electricity in coulombs which must be passed through the electrolyte in order to produce or dissolve one gram equivalent of any substance at the electrode.* The best value of $\mathcal{F}$, so far obtained, is 96495·6±1·1 coulombs but for all practical purposes its value is taken to be 96500 coulombs. Thus,

$$\mathcal{F} = 96500 \text{ coulombs}$$

Putting this value of $\mathcal{F}$ in Eq. (5·4), we get

$$m = \frac{I \times t \times E}{96500} \qquad \text{...(5·5)}$$

If $I \times t$ is put equal to 1 in Eq. (5·5), then

$$m = \frac{E}{96500} = Z$$

where Z is known as **electrochemical equivalent** of the substance, and is defined as *the amount of substance produced or dissolved when 1 coulomb of electricity has passed through the solution.*

Putting Z for $E/96500$ in Eq. (5·5) we get

$$m = Z \times I \times t \qquad \text{...(5·6)}$$

which is the quantitative formulation of the first law.

Example 1. *How many amperes of electricity should be passed through a solution of silver nitrate for an hour so that 60·3 gm of silver is deposited at the cathode? The equivalent weight of silver is 107·87.*

Solution. We know that

$$m = \frac{I \times t \times E}{96500}$$

Here $m = 60·3$ gm

$t = 1 \times 60 \times 60 = 3600$ sec

$E = 107·87$

$$\therefore 60·3 = \frac{I \times 3600 \times 107·87}{96500}$$

or $$I = \frac{60·3 \times 96500}{3600 \times 107·87} = 14·98 \text{ amp}$$

Coulometers. The exact relationship between the amount of chemical change and the quantity of electricity passed through electrolyte given by Faraday's laws has been made the basis of measuring the quantity of electricity by an electrochemical method. An apparatus used for such a purpose is known as **coulometer.** There are many coulometers but only those which possess high degree of accuracy are used. For an accurate work, **silver coulometer** is generally used, a convenient form of which is shown in Fig. 5·2. It consists of

a platinum dish or cup which serves as cathode and is filled with aqueous solution of pure silver nitrate as electrolyte. The anode is a block of pure silver enclosed in a porous pot PP' which prevents detached particles of silver from anode, if any, to fall on cathode. At the start of the electrolysis, the platinum cup is washed, dried and weighed. After electrolysis, the electrolyte is removed and the platinum cup with its deposits is then washed, dried, and weighed. The increase in weight is equal to the amount of silver deposited during electrolysis. Using the fact that one gm equivalent *i.e.*, 107.17 gm silver is deposited by 96500 coulombs of electricity, the quantity of electricity passed can be calculated from the amount of silver deposited. This is how the quantity of current is measured. Other coulometers, such as, copper coulometer, iodine coulometer and water coulometer are also used.

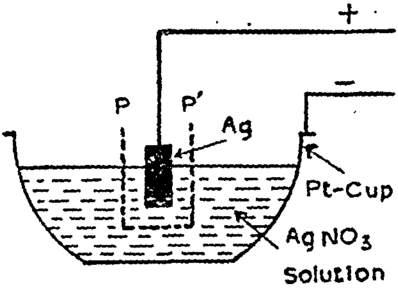


Fig. 5·2 Silver Coulometer

MIGRATION OF IONS

The conduction of electricity in electrolyte is due to the migration of ions-positive ions *i.e.*, **cations** moving towards cathode and negative ions *i.e.*, **anions** moving towards anode. The migration of ions can be demonstrated by a simple experiment shown in Fig. 5·3.

A U-tube is half filled with purple coloured aqueous solution of copper permaganate, $Cu(MnO_4)_2$. The solution contains hydrated Cu^{2+} ions of blue colour and MnO_4^- ions of purple colour. A colourless aqueous HNO_3 is allowed to float on the top of $Cu(MnO_4)_2$ solution in both the limbs. An electrode is dipped in HNO_3 solution in each of the limb and electric field is applied by joining the two electrodes to the two terminals of a battery.

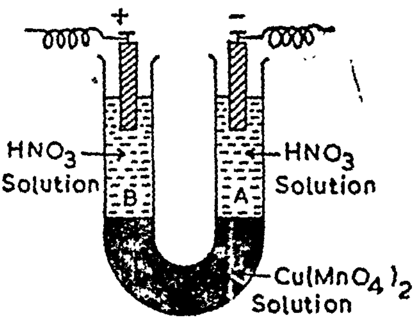


Fig. 5·3. Migration of Ions under an Electric fielp.

After some time, blue colour, characteristic of Cu^{2+} is observed moving in region A, while the purple colour characteristic of MnO^-_4 ions is seen moving in region B. These observations indicate the simultaneous migration of cations and anions towards cathode and anode respectively.

A careful observation of the displacement of these coloured ions indicates that Cu^{2+} and MnO^-_4 ions migrate with different speeds. The migration speed of an ion depends upon (*i*) the nature

of the ion (*ii*) the temperature, and (*iii*) the voltage applied. With the increase in the temperature and applied voltage, there is increase in the migration speeds of ions.

Relative Speeds of Ions.

Although the speeds of cations and anions are unequal, they are discharged in equivalent amounts at the appropriate electrodes. The change in concentration in the two electrode regions would be different depending upon the speeds of ions. These facts were explained by Hittorf in a simple way.

Consider an electrolytic cell divided into three compartments as shown in Fig. 5·4. These compartments are divided by imaginary partitions P and Q permeable to ions. The electrodes are placed in the two extreme compartments. The compartment having anode is called **anode compartment** and that having cathode as **cathode compartment.** The electrolyte contains equivalent number of cations and anions represented by + and − signs respectively. The

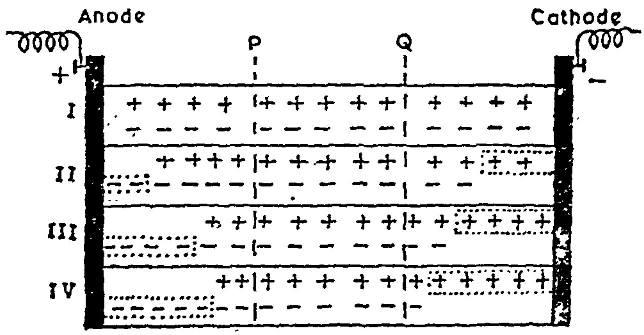


Fig. 5·4. Concentration changes due to Migration of Ions.

system before electrolysis is represented by I, which contains 13 pairs of ions in all the three compartments. Four of these pairs are preeent in each of the cathode and anode compartment and five pairs in the middle compartment. On applying potential the cations move towards cathode and anions towards anode. The following cases may be considered depending on the different speeds of cations and anions :

Case (*i*) *When only anions move and cations remain stationary.* Suppose in a given time two anion have migrated from the cathode through middle, to the anode compartment. This situation is represented by II in the figure. Now two unpaired anions are present in the anode compartment and the same number of unpaired [illegible] are present in the cathode compartment. Hence these unpaired [illegible] ons and cations are discharged at the anode and cathode [illegible]. Thus, the cathode compartment has suffered a loss of [illegible] and two anions, while there is no change in the [illegible]

ment. It should be noted that the same number of ions are discharged at the electrodes, though only anions moved and cations remained stationary.

Case (*ii*) *When cations and anions move with the same speed.* In a given time suppose two cations move towords cathode, then in the same time two anions will move towards anode. This situation is represented by III in the figure. In this case also the same number, i.e., four cations and four anions will be discharged at the electrodes. Thus, each compartment nas suffered a loss of two cations and two anions.

Case (*iii*). *When cations and anions move with different speeds.* Let the speeds of the ions be such that when three anions move towards anode in a given time, two cations move towards cathode. This situation is represented by IV in the figure. In this case also the same number of unpaired ions. *i.e.*, five of each type will be discharged at the electrodes, though the speeds of ions are different. Thus, the anode compartment has suffered a loss of two anions and two cations and the cathode compartment has suffered a loss of three anions and three cations.

From the above discussions we conclude :

(*i*) Concentration of the middle compartment remains unchanged.

(*ii*) The ions are always discharged in equivalent amounts at the electrodes irrespective of their speeds.

(*iii*) The number of units of ions lost in any electrode compartment is directly proportional to the speed of ion leaving that compartment. These units are expressed in **gm equivalents** or **equivalents**. Thus, the loss of equivalents of electrolyte in anode compartment is proportional to the speed of cation and that in cathode compartment is proportional to the speed of anion. Hence.

$$\frac{\text{Equivalents of electrolyte lost from anode compartment}}{\text{Equivalents of electrolyte lost from cathode compartment}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} \quad (5{\cdot}7)$$

(*iv*) The number of equivalents of a substance liberated at anode or cathode is equal to the sum of the number of equivalents of tte electrolyte lost from both the compartments.

Transport Number.

The electric current through an electrolyte is carried by the stream of cations and anions. As the cations and anions move with different speeds, their shares in the transportation of current are also

different. *The ~~formation~~ fraction of the total current carried across by a particular type of ion is called its* **transport number** or **transference number** or **Hittorf number.** If u_+ and u_- are the speed of cations and anions respectively then the total current passed through an electrolyte, under given conditions, is proportional to $(u_+ + u_-)$. The quantity of electricity carried by cation is proportional to u_+ and that by anion is proportional to u_-. Thus the fraction of the total current carried by cation is $u_+/u_+ + u_-$ and that by anions is $u_-/u_+ + u_-$. These fractions are termed as **transport numbers of cation** (t_+) and **anion** (t_-) respectively. Thus,

$$t_+ = \frac{u_+}{u_+ + u_-} \qquad ...(5{\cdot}8)$$

$$t_- = \frac{u_-}{u_+ + u_-} \qquad ...(5{\cdot}9)$$

From Eq. (5·8) and Eq. (5·9), we obtain

$$t_+ + t_- = \frac{u_+}{u_+ + u_-} + \frac{u_-}{u_+ + u_-} = 1 \qquad ...(5{\cdot}10)$$

Dividing Eq. (5·8) by Eq. (5.9), we get

$$\frac{t_+}{t_-} = \frac{u_+}{u_-} \qquad ...(5{\cdot}11)$$

Experimental Determination of Transport Number

The following three methods are generally employed to determine the transport numbers :

(i) Hittorf method
(ii) Moving boundary method
(iii) EMF method.

(i) **The Hittorf Method.** As already discussed, the number of gm equivalents of an electrolyte lost from an electrode compartment is proportional to the speed of ion leaving that compartment. Hence,

Equivalents of electrolyte lost from anode compartment $\propto u_+$ ...(5·12)

Equivalents of electrolyte lost from cathode compartment $\propto u_-$ ...(5·13)

∴ Equivalents of electrolyte lost from both compartments $\propto u_+ + u_-$ ...(5·14)

Dividing Eq. (5·12) by Eq. (5·14), we get

$$\frac{\text{Equivalents of electrolyte lost from anode compartment}}{\text{Equivalents of electrolyte lost from both compartments}} = \frac{u_+}{u_+ + u^-} \qquad ...(5{\cdot}15)$$

Since $\frac{u_+}{u_+ + u_-} = t_+$, the transport number of cation, Eq. (5·15) can be written as

$$t_+ = \frac{\text{Equivalents of electrolyte lost from anode compartment}}{\text{Equivalents of electrolyte lost from both compartments}} \quad ...(5\cdot16)$$

Since the equivalents of electrolyte lost from both the compartments are equal to the number of equivalents deposited on each electrode, Eq. (5·16) can be written as

$$t_+ = \frac{\text{Equivalents of electrolyte lost from anode compartment}}{\text{Equivalents deposited on each electrode}} \quad ...(5\cdot17)$$

The equivalents deposited on an electrode can be determined by inserting a silver or copper coulometer in the circuit. According to Faraday's laws, the equivalents deposited on an electrode will be equal to the equivalents of metal deposited on the cathode of coulometer. Hence Eq. (5·17) can be written as

$$t_+ = \frac{\text{Equivalents of electrolyte lost from anode compartment}}{\text{Equivalents of metal deposited in coulometer}} \quad ...(5\cdot18)$$

Similarly,

$$t_- = \frac{\text{Equivalents of electrolyte lost from cathode compartment}}{\text{Equivalents of metal deposited in coulometer}} \quad ...(5\cdot19)$$

These expressions form the basis of determining the transport number by Hittorf method. Thus, the determination of transport number involves the measurements of

(*i*) the number of equivalents lost from the cathode or anode compartment, and

(*ii*) equivalents of metal deposited in coulometer.

A commonly used form of Hittorf apparatus is shown in Fig. 2·5. It consists of two vertical glass tubes A and B which are connected by a U-tube T. Tubes A and B represent cathode and anode compartments respectively and tube T constitutes the middle compartment. Each tube has a stop cock at the bottom and the U-tube is also provided with two pinch-cocks x and y. The whole apparatus is filled with a solution of an electrolyte of known concentration. Electrodes of suitable metal are inserted into A and B and are connected in series with milli-ammeter M, coulometer C, a

variable resistance R, and a battery. The electrodes are enclosed in

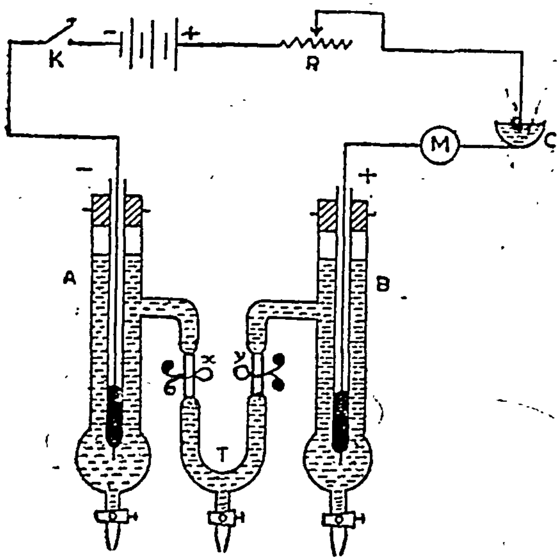


Fig. 5·5 Transport Number Apparatus for Hittorf Method.

a stout glass tube and a very small portion of the metal is ejected in solution in the lower part of the glass tube as shown in the Fig.

A current of about 10—20 milliamperes is passed through the electrolyte for about 2—3 hours so that an appreciable change in concentration round the electrodes may take place. Too large changes in concentration should be avoided. After electrolysis the pinch-cocks x and y are closed to isolate the three compartments. The solutions from all the three compartments are withdrawn in separate dried and weighed flasks. The flasks with solutions are again weighed and the solutions analysed. The solution of middle compartment should show no change in concentration. If it has changed, the excess current has been passed and the experiment should be repeated.

From the analysis, the gm equivalents of electrolyte for a definite weight of solvent in an electrode compartment can be obtained. The amount of metel deposited on the cathode in coulometer is also determined.

Simple general formulae can be obtained for the computation of transport numbers. During electrolysis the change in equivalents of ions in an electrode compartment is due to two factors : (*i*) migration of ions, and (*ii*) electrode reaction. This can be illustrated by taking an example of electrolysis of $AgNO_3$ using Ag electrodes. Let N_I and N_F be the gm equiv. of $AgNO_3$ associated with a *definite weight* of water in the anode compartment before

and after electrolysis respectively. Let N_E be the gm equiv. of the metal deposited in a coulometer.

In this case, the electrode reaction takes place in the anode compartment. NO_3^- ions attack the Ag anode and form N_E gm equiv of $AgNO_3$ (Faraday's laws.

Had there been no migration of Ag^+ ions, the total number of gm equiv of Ag^+ ions in the anode compartment would have been equal to $(N_I + N_E)$.

But the actual number of gm equiv of Ag^+ ions present $= N_F$.

$\therefore$ Number of gm equiv of Ag^+ ion lost from the anode compartment $= N_I + N_E - N_F$. ...(5·20)

The gm. equiv of metal deposited in coulometer $= N_E$

$\therefore$ Transport number of Ag^+ ion,

$$t_+ = \frac{N_I + N_E - N_F}{N_E} \qquad \text{...(5·21)}$$

Since $\quad t_+ + t_- = 1$

Transport number of NO_3^- ions,

$$t_- = 1 - t_+$$

$$= 1 - \frac{N_I + N_E - N_F}{N_E}$$

$$= \frac{N_F - N_I}{N_E} \qquad \text{...(5·22)}$$

In case of unattackable electrodes, *e.g.*, electrolysis of $AgNO_3$ between Pt electrodes Eq. (5·21) takes a different form. In this case, since there is no electrode reaction, no Ag^+ ions will be formed in the anode compartment due to the attack of NO_3^- ions. Thus, the value of N_E in Eq. (5·20) will be zero. Hence

Number of gm equiv of Ag^+ ions lost from anode compartment
$= N_I - N_F$ ...(5·23)

The gm equiv of metal deposited $= N_E$

$\therefore$ Transport number of Ag^+ ion,

$$t_+ = \frac{N_I - N_F}{N_E} \qquad \text{...(5·24)}$$

and transport number of NO_3^- ion,

$$t_- = 1 - t_+$$

$$= 1 - \frac{N_I - N_F}{N_E}$$

$$= \frac{N_E - N_I + N_F}{N_E} \qquad \ldots(5{\cdot}25)$$

Equations (5·21) and (5·24) are employed in computing transport numbers of cations, and Eqs. (5·22) and (5·25) are used in computing transport numbers of anions.

Example 2. *A solution of silver nitrate containing, 1·085 gm of silver nitrate per 101·085 gm of solution was electrolysed between silver electrodes. After electrolysis the whole of the anode solution was removed which weighed equal to 27·45 gm. On analysis, it was found that it contained 0·3608 gm of silver nitrate. The mass of copper deposited in a copper coulometer in series was found to be 0·0234 gm. Calculate the transport number of silver and nitrate ions.* (*Eq. weight of* $AgNO_3$ = *169·87 and Cu = 31·77*)

Solution. In this case where electrode reaction occurs, we know that

$$t_+ = \frac{N_I - N_F + N_E}{N_E}$$

(*i*) *Calculation of N_F*

After electrolysis, the weight of silver nitrate in 27.45 gm of solution = 0·3608 gm.

$\therefore$ weight of water = 27·45—0·3608 = 27·0892 gm

$\therefore$ Amount of silver nitrate in 27·0892 gm water = 0·3608 gm

$$= \frac{0{\cdot}3608}{169{\cdot}87} \text{ gm equiv}$$

$$= 0{\cdot}002123 \text{ gm equiv}$$

The number of gm equiv of silver will also be the same

$\therefore$ N_F = 0·002123 gm equiv

(*ii*) *Calculation of N_I*

Initially the weight of silver nitrate in 101·085 gm of solution = 1·085 gm

$\therefore$ weight of water = 101·085—1·085 = 100 gm

$\therefore$ Amount of silver nitrate present initially in 27·0892 gm of water

$$= \frac{1{\cdot}085 \times 27{\cdot}0892}{100} \text{ gm}$$

$$= \frac{1.085 \times 27{\cdot}0892}{100 \times 169{\cdot}87} \text{ gm equiv}$$

$$= 0{\cdot}0017304 \text{ gm equiv}$$

The number of gm equiv of silver will also be the same

$\therefore$ N_I = 0·001730 gm equiv

(*iii*) *Calculation of N_E*

The amount of copper deposited in coulometer = 0·0234 gm

$$= \frac{0{\cdot}0234}{31{\cdot}77} \text{ gm equiv}$$

= [illegible]

$\therefore \quad N_E = 0{\cdot}0007364$ gm equiv

$\therefore \quad t_+ = \dfrac{0{\cdot}001730 - 0{\cdot}002123 + 0{\cdot}0007364}{0{\cdot}0007364} = \dfrac{0{\cdot}0003434}{0{\cdot}0007364}$

$= 0{\cdot}4663$

Since $t_- = 1 - t_+$

$= 1 - 0{\cdot}4663 = 0{\cdot}5337$

$\therefore$ The transport number of Ag^+ ion $= 0{\cdot}4663$
and the transport number of NO_3^- ion $= 0{\cdot}5337$

Example 3. *A solution containing 7·39 gm silver nitrate per 1000 gm water was electrolysed between platinum electrodes. After electrolysis it was found that 23·2520 gm of anode solution contained 0·1120 gm of silver nitrate. In a silver coulometer in series, 0·0805 gm. silver was deposited. Calculate the transport numbers of silver and nitrate ions. (Eq. weight of Ag NO_3 = 169·87 and Ag = 107·87)*

Solution. In this case where electrodes are inert we know that:

$$t_+ = \frac{N_I - N_F}{N_E}$$

(*i*) *Calculation of N_F*

After electrolysis the weight of silver nitrate in 23·2520 gm of solution $= 0{\cdot}1120$ gm

$\therefore$ Weight of water $= 23{\cdot}2520 - 0{\cdot}1120 = 23{\cdot}140$ gm

$\therefore$ Amount of silver nitrate in 23.14 gm water $= 0{\cdot}1120$ gm

$= \dfrac{0{\cdot}1120}{169{\cdot}87}$ gm equiv

$= 0{\cdot}0006592$ gm equiv

The number of gm equiv of silver will be the same

$\therefore \quad N_F = 0{\cdot}0006592$ gm equiv

(*ii*) *Calculation of N_I*

Initially the weight of silver nitrate in 1000 gm water $= 7{\cdot}39$

$\therefore$ Amount of silver nitrate present initially in 23·140 gm water

$= \dfrac{7{\cdot}39 \times 23{\cdot}140}{1000}$ gm

$= \dfrac{7{\cdot}39 \times 23{\cdot}140}{1000 \times 169{\cdot}87}$ gm equiv

$= 0{\cdot}001007$ gm equiv

The number of gm equiv of silver will also be the same

$\therefore \quad N_I = 0{\cdot}001007$ gm equiv

(*iii*) **Calculation of N_E**

The amount of silver deposited in coulometer $= 0{\cdot}0805$ gm

$= \dfrac{0{\cdot}0805}{107{\cdot}87}$ gm equiv

$= 0{\cdot}0007463$ gm equiv

$\therefore \quad N_E = 0{\cdot}00074133$ gm equiv

Hence $t_+ = \dfrac{0{\cdot}001007 - 0{\cdot}00065923}{0{\cdot}0007463} = \dfrac{0{\cdot}00034777}{0{\cdot}0007463}$

$= 0{\cdot}466$

Since $t_- = 1 - t_+$
$= 1 - 0{\cdot}466 = 0{\cdot}534$

$\therefore$ transport number of Ag^+ ion $= 0{\cdot}466$
and the transport number of NO_3^- ions $= 0{\cdot}534$

Example 4. *In an electrolysis of copper sulphate solution between copper electrodes, the total mass of copper deposited at the cathode was found to be 0·528 gm. The masses of copper associated with a definite weight of water in whole of the anode solution before and after electrolysis were found to be 2·0 gm and 2·33 gm respectively. Calculate the transport numbers of copper and sulphate ions. (Eq. weight of Cu=31·77).*

Solution. In this case where electrode reaction occurs we know that

$$t_+ = \frac{N_I - N_F + N_E}{N_E}$$

(*i*) *Calculation of N_F*

After electrolysis the weight of copper in whole of the anode solution

$= 2{\cdot}33$ gm

$= \frac{2{\cdot}33}{31{\cdot}77}$ gm equiv

$$\therefore N_F = \frac{2{\cdot}33}{31{\cdot}77} \text{ gm equiv}$$

(*ii*) *Calculation* of N_I

Before electrolysis the weight of copper in whole of the anode solution $= 2{\cdot}0$ gm

$$= \frac{2{\cdot}0}{31{\cdot}77} \text{ gm equiv}$$

$$\therefore N_I = \frac{2{\cdot}0}{31{\cdot}77} \text{ gm equiv}$$

(*iii*) **Calculation of N_E**

The amount of copper deposited on cathode $= 0{\cdot}528$ gm

$= \frac{0{\cdot}528}{31.77}$ gm equiv

$$\therefore N_E \frac{0{\cdot}528}{31{\cdot}77} \text{ gm equiv}$$

$$\text{Hence } t_+ = \frac{\frac{2{\cdot}0}{31{\cdot}77} - \frac{2{\cdot}33}{31{\cdot}77} + \frac{0{\cdot}528}{31{\cdot}77}}{\frac{0{\cdot}528}{31{\cdot}77}}$$

$$= \frac{2{\cdot}0 - 2{\cdot}33 + 0{\cdot}528}{0{\cdot}528} = \frac{0{\cdot}198}{0{\cdot}528}$$

$$= 0{\cdot}375$$

Since $t_- = 1 - t_+$
$= 1 - 0{\cdot}375 = 0{\cdot}625$

$\therefore$ The transport number of Cu^{++} ions $= 0{\cdot}375$
and the transport number of SO_4^{--} ions $= 0{\cdot}625$

(iii) **Moving Boundary Method.** The Hittorf method, though simple in principle, suffers from several drawbacks. Due to diffusion and convection there is always a mixing of solutions to some extent, so accurate results cannot be obtained. Also due to electrolysis the concentration of the electrolyte changes and the values of transport number so obtained do not pertain to a definite concentration of the electrolyte. Further, low current is passed for a prolonged time with the result that the electrolysis is slow and the process is time consuming. Hence a more convenient and accurate method, known as moving boundary method, is now generally used for the determination of transport number.

The moving boundary method is based on the direct observation of the movement of boundary between two ionic solutions under an applied potential. To understand this method let us take a specific example of the determination of transport number of a cation, say H^+ ion in HCl solution. For this purpose it is essential to have another solution of an electrolyte commonly known as **indicator electrolyte.** The indicator electrolyte, in this case, should be such that (*i*) it should have common anion, *i.e.*, Cl^- ion, and (*ii*) the speed of its cation should be less than speed of H^+ ion in HCl solution. A suitable electrolyte fulfilling both the conditions is $CdCl_2$ solution because it has Cl^- ion and the speed of Cd^+ ion is less than that of H^+ ion.

The apparatus used is shown in Fig. 5·6. It consists an electrolytic cell the middle portion of which is in the form of a vertical tube PQ of a uniform bore. The cell is filled with HCl and $CdCl_2$ solutions in the manner as shown in the figure. With the help of a device (not shown in figure) a sharp boundary between these solutions is produced at *x*. The concentration of $CdCl_2$ solution should be such that its density is higher than that of HCl solution so that it remains below the HCl solution. A Pt cathode is inserted at the top, while the anode, made of Cd stick is inserted at the bottom. The electrodes are joined through a battery B, variable reistance R, milliammeter M, and coulometer C in series.

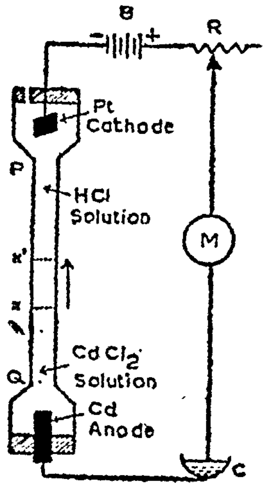


Fig. 5·6 Transport Numbers by Moving Boundary Method.

When the current is passed, H^+ and Cd^+ ion move upwards towards the cathode. Since slowly moving Cd^{2+} ions can never overtake the fastmoving H^+ ions, the sharap boundary between the two solutions is preserved and moves gradually upwards. By knowing the quantity of electricity passed and the volume swept out by the boundary the transport number can be calculated as follows :

Suppose Q faradays of electricity have passed through the solution and the boundary has moved from x to x . The displacement of the boundary is measured accurately with the help of a cathetometer. Let the displacement be l cm. If the cross-section of the tube PQ is a sq cm, then the volume swept out by the boundary in moving l cm is $l \times a$ cc. Further, if the concentration of HCl solution (or H^+ ion) is c gm equivalents per litre, then the amount of HCl (or H^+ ion) in the volume swept out will be $l \times a \times c/1000$ gm equivalents.

Since Q faradays of electricity have been passed, the fraction carried by H^+ ions will be equal to $t_+ \times Q$ faradays. Since one gm equivalent carries one faraday of electricity, $t_+ \times Q$ gm equivalents of H^+ ions must have migrated from x to x'

$$\therefore \; t_+ \times Q = \frac{l \times a \times c}{1000}$$

$$\text{or} \qquad t_+ = \frac{l \times a \times c}{1000 \times Q} \qquad ...(5\cdot26)$$

Example 5. *A moving boundary experiment was performed at 25°C with 0·02 N HCl using $CdCl_2$ as indicator solution. A constant current of 0·6016 amp was passed for 1035 sec which moved the boundary through 6·34 cm in the tube of cross sectional area 0·1115 cm². Calculate the transport numbers of H^+ and Cl^- ions.*

Solution. We know that

$$t_+ = \frac{l \times a \times c}{100 \times Q}$$

Here

$$l = 6\cdot34$$

$$a = 0\cdot1115 \text{ cm}^2$$

$$c = 0\cdot02 \text{ gm equiv lit}^{-1}$$

$$Q = \frac{\text{amp} \times \text{sec}}{96500} = \frac{0\cdot0016 \times 1035}{96500} \text{ faraday}$$

$$\therefore \qquad t_+ = \frac{6\cdot34 \times 0\cdot1115 \times 0\cdot02}{1000 \times 0\cdot016 \times 1035/96500}$$

$$= \frac{6\cdot34 \times 0\cdot1115 \times 0\cdot02 \times 96500}{1000 \times 0\cdot0016 \times 1035}$$

$$= 0.8239$$

Since

$$t_- = 1 - t_+$$

$$= 1 - 0\cdot8239 = 0\cdot1761$$

$\therefore$ The transport number of H_+ ions $= 0\cdot8239$

and the transport number of Cl^- ions $= 0\cdot1761$

(iii) **EMF Method.** The emf method for the determination of transport number will be discussed in chapter 7.

Some Results of Transport Number Measurements

Experimental studies have revealed the following facts :

1. The values of transport number do not depend upon the applied emf and the current strength.

2. Transport number of an ion is not constant and depends upon the nature of other ion associated with it, *i.e.*, transport number of Na^+ ion in NaCl, $NaNO_3$, NaBr are different. Similarly the transport numbers of Cl^- in HCl, NaCl, and KCl are different.

3. The transport numbers of ions vary only slightly with change in concentration.

4. With increase in temperature the transport number of cations and anions change, each tending to approach a value of 0·5.

5. The lesser the ion is hydrated, more would be its transport number.

CONDUCTANCE OF SOLUTIONS

Conductance. Like metallic conductors electrolytic conductors also obey Ohm's law,

$$I = \frac{\mathcal{E}}{R} \qquad ...(5\cdot27)$$

where I is the current in amperes, $\mathcal{E}$ is the applied potential in volts and R is the resistance in ohms. This shows that for a given voltage, the strength of current passed through the conductor depends on its resistance.

In case of electrolytic conductors it is convenient to use the term conductance in place of resistance. **Conductance** *is the reciprocal of resistance.* It is generally denoted by L. Thus,

$$L = \frac{1}{R} \qquad ...(5\cdot28)$$

The conductance, being reciprocal of resistance, indicates the ease with which the current flows in the electrolyte. Since the resistance is expressed in ohms, conductance is expressed in **ohm⁻¹** or **mhos** or **reciprocal ohms (ro)**.

Specific Conductance or Conductivity.

The resistance R offered by any uniform conductor (metallic or solutions of electrolyte) is directly proportional to its length l and inversely proportional to its cross-sectional area a. Thus,

$$R \propto \frac{l}{a}$$

or

$$R = \rho\frac{l}{a} \qquad ...(5\cdot29)$$

where ρ is the proportionality constant and is known as **specific resistance** or **resistivity.** The value of ρ depends on the nature of conductors. *The reciprocal of specific resistance or resistivity*

called **specific conductance** or **conductivity** and is generally denoted by κ (*kappa*). Thus,

$$\kappa = \frac{1}{\rho} \qquad \ldots(5\cdot30)$$

Eq. (5·29) can be written as

$$\frac{1}{R} = \frac{1}{\rho} \cdot \frac{a}{l}$$

Since $\frac{1}{R} = L$ and $\frac{1}{\rho} = \kappa$, we get

$$L = \kappa \frac{a}{l} \qquad \ldots(5\cdot31)$$

If two electrodes P and Q of 1 sq cm cross-sectional area are placed 1 cm apart in a solution of an electrolyte as shown in Fig. 5·7, then the solution between the two electrodes will be in the form of a cube of 1 cm edge. In this case a=1 sq cm and $l=1$ cm. Putting these values in Eq. (5 31), we obtain

$$L = \kappa \qquad \ldots(5\cdot32)$$

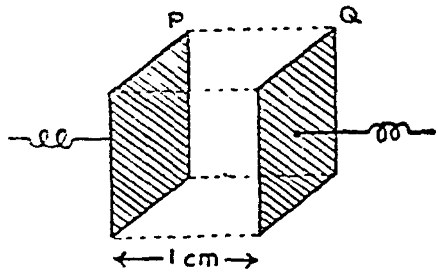


Fig 5·7

Thus, the **specific conductance** or **conductivity** is defined as *the condnctance of a solution between two electrodes of 1 sq cm cross-sectional area placed 1 cm apart*. Since the units of specific resistance are ohm cm, the units of specific conductance are ohm $^{-1}$ cm^{-1}.

The current in a electrolyte is carried solely by ions and hence the conductance or specific conductance depends on the concentration of the electrolyte in solution. In order to compare conductances of various electrolytes concentration factor should be included and hence solutions having chemically comparable amounts of substances, *e.g.*, equivalent or equimolecular quantities should be used. It is for this reason that the concepts of equivalent conductance and molar conductance are generally used.

Equivalent and Molar Conductances

The **equivalent conductance** of an electrolyte is defined as *the conductance of the solution containing 1 gm equivalent of the dissolved electrolyte, when the entire solution is placed betwe— two sufficiently large parallel electrodes kept 1 cm a*

equivalent conductance is *the conductance due to all the ions produced by 1 gm equivalent of the electrolyte in solution.* It is denoted by Λ.

The direct determination of equivalent conductance is not practicable. It is calculated from specific conductance in the following way. Suppose 1 cc of a solution containing 1 gm equivalent of the electrolyte is placed between two electrodes kept 1 cm apart. The conductance of this solution is equal to equivalent conductance because it contains 1 gm equivalent of the electrolyte. This conductance is also equal to specific conductance because 1 cc of solution is enclosed by two electrodes placed 1 cm apart so that the area of each electrode covered by the solution is 1 sq cm.

Again, if 16 cc solution containing 1 gm equivalent of the electrolyte is placed between two electrodes P and Q kept 1 cm apart as shown in Fig. 5·8, then the conductance of the solution will be equal to the equivalent conductance, but it will not be equal to specific conductance. This is because that the given solution is now divided into 16 cubes, each with 1 cm edge, between the electrodes. Conductance due to each cube is equal to specific conductance, hence the conductance of the solution is equal to 16 times the specific conductance. In other words, we can say that the conductance of the solution is equal to the specific conductance multiplied by the volume in cc containing 1 gm equivalent of the electrolyte. Since conductance, in this case, is equal to equivalent conductance, we may conclude that

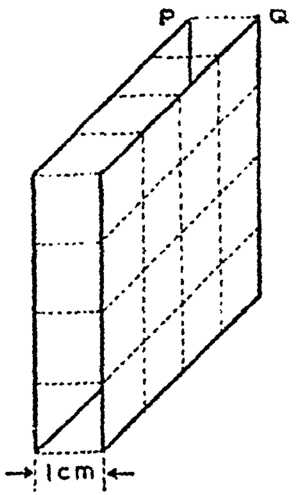


Fig. 6·8

Equivalent conductance = Specific conductance × Volume in cc containing 1 gm equiv of the electrolyte.

or $$\Lambda = \kappa \times V \qquad ...(5{\cdot}33)$$

Thus, **equivalent conductance** *may also be defined as the specific conductance multiplied by the volume in cc containing 1 gm equivalent of the electrolyte.*

If c is concentration in terms of gm equiv lit^{-1}, then

$$V = 1000/c$$

Putting this value of V in Eq. (5·33) we get

$$\Lambda = \frac{1000\kappa}{c} \qquad ...(5{\cdot}34)$$

The units of equivalent conductance are ohm^{-1} cm^2 equiv^{-1}.

If the concentration is expressed in terms of moles/litre, than the term **molar conductance** is used like equivalent conductance. The **molar conductance** may be defined as *the specific conductance multiplied by the vclume in cc containing* 1 *mole of the electrolyte.* It is usually denoted by μ. Thus,

$$\mu = \kappa \times V = \frac{1000\ \kappa}{c} \qquad ...(5{\cdot}35)$$

The units of molar conductance are ohm^{-1} cm^{2} mole^{-1}.

Experimental Determination of the Conductance of an Electrolyte.

Since the conductance of a solution is the reciprocal of its resistance, it can be determined by measuring the resistance of the solution. The solution is taken in a vessel known as **conductance cell.**

A conductance cell is a vessel of highly insoluble glass, such as pyrex or quartz and is fitted with two parallel electrodes made of stout Pt foil. The electrodes are fused in glass tubes and their connections are made by placing some Hg in the tube. The position of the electrodes should be kept fixed so that the distance between them does not change during the measurement. The electrodes should be freshly coated with layer of finely divided Pt black before the experiment to reduce polarization of the electrodes. The deposition is done by the electrolysis of platinic chloride. Out of various types of cells differing in size and shape, three commonly used are shown in Fig. 5·9. In the cell (*a*) the electrodes are adjustable by fixing the glass tubes in the ebonite cover. Cells (*b*) and (*c*) have electrodes

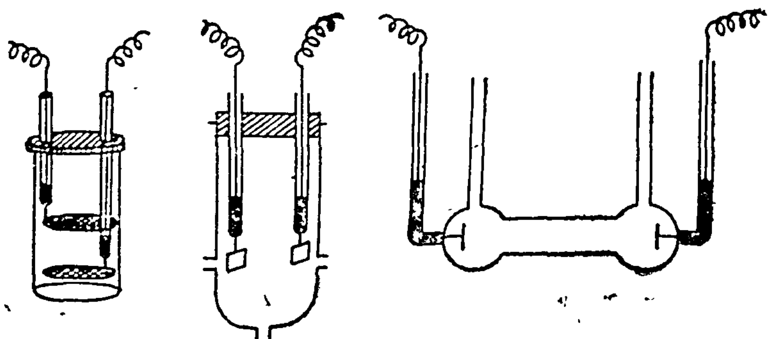

(a) (b) (c)

Fig. 5·9. Conductance Cells.

at a fixed distance. The distance between the electrodes in (*b*) is comparatively lesser and is generally used for low conducting solutions. Cell (*c*), having electrodes at a relatively larger distance is used for high conducting solutions.

The resistance of the solution can be measured by the well known Wheatstone's meter bridge method with some

The modifications have been done because the direct current causes the electrolysis and the following complications arise :

(*i*) The concentration of the electrolyte changes at the electrodes, and

(*ii*) Polarization (back emf) sets in due to the accumulation of products at the electrodes.

To overcome these difficulties the alternating current is used in place of direct current. A.C. current of the frequency of 1000-3000 cycles/sec is generally used. This can be obtained from induction coil for less accurate work and vaccum tube oscillator for highly accurate work. When alternating current is used, the determination of null point cannot be made by ordinary galvanometer, hence galvanometer is replaced by head phone or magic eye.

A convenient form of an alternating current Wheatstone bridge is shown in Fig. 5·10. AB is uniform wire made of platinum-iridium alloy and stretched over a meter scale. A sliding contact X moves

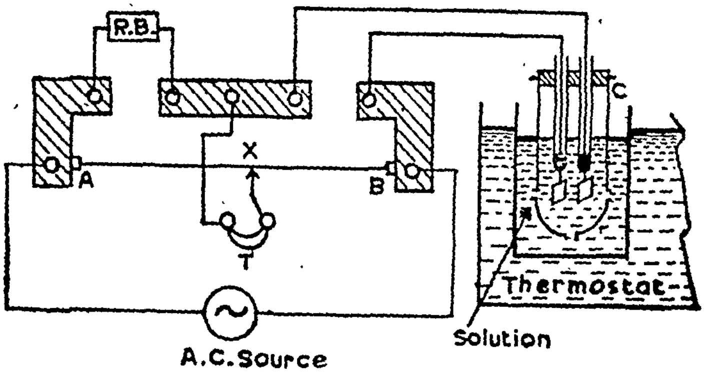


Fig. 5·10. Determination of Conductance of Electrolyte

over the wire. R.B. is the resistance box for introducing resistance in the bridge. C is the conductance cell. The cell should be placed in a thermostat to maintain the temperature constant. A suitable source of alternating current is connected to the bridge. T is the head phone to detect the null point.

The solution of the electrolyte whose conductance is to be determined is filled in the conductance cell and connected to the bridge as shown in the figure. The resistance R in the resistance box is properly adjusted and the sliding contact is moved over the wire until minimum sound is detected in the head phone. This is the null point. At the null point the bridge is balanced and the following relation applies:

$$\frac{\text{Resistance of solution in the cell}}{\text{Resistance } R} = \frac{\text{Length BX}}{\text{Length AX}} \quad \ldots(5{\cdot}36)$$

Since the resistance R, and lengths BX and AX are known, the resistance and hence the conductance of the solution can be obtained.

Now a days very sophisticated instruments are made in which cathode ray oscilloscope or magic eye is used as an indicator of null point. These apparatus directly read resistance and conductaace of the solution.

It should be noted that for the accurate determination of conductance, the solution of electrolyte should be made in extremely purified water known as **conductance water** which has no conductance due to impurities. Conductance water can be obtained by passing distilled water through an ion-exchange resin. For ordinary experimental work, it can be obtained by redistilling the distilled water containing a pinch of $KMnO_4$ in a distillation apparatus made of resistance glass. The middle fraction of the distillate is collected and stored in a vessel made of resistance glass.

Determination of Specific Conductance.

The specific conductance is related to the conductance by the following relation

$$\kappa = L \frac{l}{a} \qquad ...(5{\cdot}37)$$

Thus, the specific conductance κ may be calculated from the observed conductance, if the value of cross-sectional area a of the electrodes and the distance between them, l, are known. It is extremely difficult to determine the value of a and l with precision. However, for a cell with fixed electrodes the factor l/a is constant. This quantity is known as **cell constant** and is represented by K. Thus,

$$K = \frac{l}{a} \qquad ...(5{\cdot}38)$$

Putting K for l/a in Eq. (5·37) we get

$$\kappa = L\,K \qquad ...(5{\cdot}39)$$

Thus, the **cell constant** may be defined as *a factor which has to be multiplied with observed conductance of the solution in order to get its specific conductance.*

Since it is difficult to obtain the area of the electrodes and the distance between them, the cell constant is determined by an indirect method. The specific conductance of KCl solution of different concentrations and at different temperatures have been precisely determined using the conductance cell of known dimensions, (*i.e.*, l and a) by many workers. Some of the accepted values are given in Table 5·1.

Table 5·1

Specific Conductances of Aqueous KCl Solutions

Concentration (*equiv lit*$^{-1}$)	*Specific Conductance* (*ohm*$^{-1}$ *cm*$^{-1}$)		
	0°C	18°C	25°C
0·01	0 0007751	0·0012227	0·0014114
0 10	0·007154	0 011192	0·012886
1·00	0·0065430	0·098200	0·111730

To determine the cell constant, the cell is filled with 0·1*N KCl* solution in conductance water and the resistance of the solution is measured at 25°C. Since the specific conductance of the solution at this temperature is known, the cell constant may be evaluated by the relation

Specific conductance = Conductance × Cell constant

or
$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Conductance}}$$

$$= \text{Specific conductance} \times \text{Resistance.}$$

or
$$K = \kappa \times R \qquad \ldots(5{\cdot}40)$$

where R is the resistance of the solution.

Once the cell constant of a cell is known, the specific conductance of a solution of any electrolyte, filled in the cell, can be determined by measuring its conductance and then multiplying it with the cell constant.

Determination of Equivalent or Molar Conductance.

To determine the equivalent or molar canductance of a solution, the specific conductance of the solution is first determined and then the equivalent or molar conductance can be evaluated from the apporopriate relation from Eqs. (5·33), (5·34) and (5·35).

Example 6. *The resistance of a conductance cell containing 0·1 N KCl solution at 25°C is 456·4 ohms. The specific conductance of 0·1 N KCl solution at 25°C is 0·012886 ohm*$^{-1}$ *cm*$^{-1}$*. Calculate the cell constant.*

Solution. We know that the cell constant K is given by

$$K = \kappa R$$

Here
$$\kappa = 0{\cdot}012886 \text{ ohm}^{-1} \text{ cm}^{-1}$$
$$R = 456{\cdot}4 \text{ ohm}$$

$$\therefore \quad K = 0.012886 \times 456.4 \text{ cm}^{-1}$$
$$= 5.882 \text{ cm}^{-1}$$

Example 7. *The resistance of a conductance cell containing 0 1 N KCl solution at 25° C was found to be 307·62 ohms. The specific conductance of 0·1 N KCl solution is known to be 0·012886 ohm⁻¹ cm⁻¹. The same cell when filled with 0·1 N Ag NO₃ solution at 25°C offered a resistance of 362·65 ohms. Calculate (i) the cell constant, (ii) the specific conductance, and (iii) the equivalent conductance of 0·1 N AgNO₃ solution.*

Solution. (*i*) *Calculation of the cell constant*

We know that

$$K = \kappa R$$

Here $\kappa = 0.012886 \text{ ohm}^{-1} \text{ cm}^{-1}$

$R = 307.62$ ohm

$$\therefore \quad K = 0.012886 \times 307.62 = 3.964 \text{ cm}^{-1}$$

(*ii*) *Calculation of the specific conductance*

We know that

$$\kappa = L \times K$$

Here $L = \dfrac{\cdot 1}{362.65} \text{ ohm}^{-1}$

$K = 3.964 \text{ cm}^{-1}$

$$\therefore \quad \kappa = \frac{3.964}{362.65} = 1.092 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

(*iii*) *Calculation of the equivalent conductance*

We know that

$$\Lambda = \frac{1000 \times \kappa}{c}$$

Here $\kappa = 1.092 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$

$c = 0.1 \text{ equiv lit}^{-1}$

$$\therefore \quad \Lambda = \frac{1000 \times 1.092 \times 10^{-2}}{0.1}$$
$$= 109.2 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ equiv.}^{-1}.$$

Example 8. *A conductance cell filled with 0·01 N solution of an electrolyte offered a resistance of 280 ohms. If the electrodes of the cell are 1·82 cm apart and have an area of cross-section equal to 4·64 sq cm, calculate (i) the specific conductance and (ii) equivalent conductance of the solution.*

Solution. (*i*) *Calculation of the specific conductance of the solution.*

We know that

$$\kappa = L \frac{l}{a}$$

Here $L = \dfrac{1}{280} \text{ ohm}^{-1}$

$l = 1.82$ cm

$$\therefore \qquad \kappa = \frac{1/280 \times 1{\cdot}82}{4{\cdot}64} = 0{\cdot}001401 \text{ ohm}^{-1} \text{ cm}^{-1}$$

(*ii*) *Calculation of the equivalent conductance of the solution.*

We know that

$$\Lambda = \frac{1000 \times \kappa}{c}$$

Here $\kappa = 0{\cdot}001401 \text{ ohm}^{-1} \text{ cm}^{-1}$

$c = 0{\cdot}01 \text{ equiv lit}^{-1}$

$$\therefore \qquad \Lambda = \frac{1000 \times 0{\cdot}001401}{0{\cdot}01}$$

$$= 140{\cdot}1 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}.$$

Example 9. *When a solution of an electrolyte of specific conductance 0·003328 ohm^{-1} cm^{-1} at 25°C was placed in a conductance cell, the resistance was found to be 314 ohms at 25°C. Calculate the cell constant. If the area of cross-section of each electrode is 1·44 sq cm, calculate the distance between the electrodes.*

Solution: (*i*) *Calculation of the cell constant*

We know that

$$K = \frac{\kappa}{L}$$

Here $\kappa = 0{\cdot}003328 \text{ ohm}^{-1} \text{ cm}^{-1}$

$$L = \frac{1}{314} \text{ ohm}^{-1}$$

$$\therefore \qquad K = \frac{0{\cdot}003328}{1/314} = 0{\cdot}003328 \times 314$$

$$= 1{\cdot}045 \text{ cm}^{-1}$$

(*ii*) *Calculation of the distance between the electrodes.*

We know that

$$K = \frac{l}{a}$$

or $l = K \times a$

Here $K = 1{\cdot}045 \text{ cm}^{-1}$

$a = 1{\cdot}44 \text{ cm}^2$

$$\therefore \qquad l = 1{\cdot}045 \times 1{\cdot}44$$

$$= 1{\cdot}505 \text{ cm.}$$

Variation of conductance with Dilution

Since the specific and equivalent conductance of a solution depend upon the number of ions, it is obvious that they depend on the concentration of the solution. It is observed that specific as well as equivalent conductance of a solution varies with the change in concentration. Table 5·2 summarizes some values of the specific and equivalent conductances of KCl solution at different concentrations at 25°C.

Table 5·2
Specific and Equivalent Conductances of Aqueous KCl Solutions at 25°C

Concentration (*equiv lit*$^{-1}$	*Dilution, i.e., Volume containing 1 gm equiv electrolyte* (*c c*)	*Specific conductance* (*ohm*$^{-1}$ *cm*$^{-1}$)	*Equivalent conductance* (*ohm*$^{-1}$ *cm*$^{-2}$ *equiv*$^{-1}$
1·0	1000	0·01119	111·90
0·1	10000	0·0012896	128·96
0·01	100000	0·00014127	141·27
0·001	1000000	0·000014695	146·95
0·005	5000000	0·000029562	147·81

It is clear from the table that the specific conductance continuously decreases, whereas the equivalent conductance continuously increases with dilution. It can be explained as follows. When the solution is diluted, the degree of dissociation of the electrolyte increases resulting in the increase in total number of ions in the solution. The volume of the solution also increases simultaneously. The increase in the volume of solution is in greater proportion than the increase in the total number of ions. Consequently, the number of ions per cc falls and hence the specific conductance decreases. Again, it is evident from the table that on dilution the decrease in specific conductance is in smaller proportion than the increase in the volume of solution containing 1 gm equivalent of electrolyte. Thus, the equivalent conductance, which is the product $\kappa \times V$, increases. The equivalent conductance increases continuously with dilution until it attains a maximum value, when the further dilution does not cause any change in the value of equivalent conductance. The maximum or limiting value of equivalent conductance is called **the equivalent conductance at infinite dilution.** It is denoted by Λ_0. At this stage the ionisation of the electrolyte is complete and the decrease of specific conductance with dilution is in the same proportion as the increase in volume containing 1 gm equivalent of electrolyte so that the product $\kappa \times V$, and hence equivalent conductance does not change.

Strong and Weak Electrolytes

The equivalent conductances of some electrolytes at different concentrations are summarized in Table 5·3.

Table 5·3

Equivalent Conductances of Aqueous Solutions of Electrolytes at 25°C

(ohm^{-1} cm^{-2} $equiv^{-1}$)

Concentration (equiv lit⁻¹)	HCl	KCl	$AgNO_3$	NaAc	Na_2SO_4	H_2SO_4	HAc	NH_4OH
1·00	332·8	111 9	—	49·1	—	—	—	—
0·10	391·32	128·96	109·14	72·80	89·98	250·8	—	3·6
0·05	399·09	133·37	115·24	76·92	97·75	272·6	7·4	5·1
0·02	407·24	138·34	121·41	81·24	106·78	308·0	11·6	8·0
0·01	412·00	141·27	124·76	83·76	112·44	336·4	16·3	11·3
0·005	415·80	143·55	127·20	85·72	117·15	364·9	22 9	16·0
0·001	421·36	146·95	130·51	88·50	124·15	399·5	49·2	34·0
0·0005	422·74	147·81	131·36	89·20	125·74	413·1	67·7	47·0

A close look at the Table 5·3 reveals that the electrolytes like HCl, KCl, H_2SO_4, $BaCl_2$, etc., have high equivalent conductance even at ordinary concentrations and with dilution the equivalent conductance increases only slightly. Such electrolytes are known as **strong electrolytes**. On the other hand, electrolytes like CH_3COOH and NH_4OH have low equivalent conductance and with dilution the equivalent conductance increases rapidly. Such electrolytes are known as **weak electrolytes.**

If the equivalent conductances of electrolytes are plotted against the square root of their concentration as shown in Fig. 5·11. two types of behaviour are observed. Plots of strong electrolytes

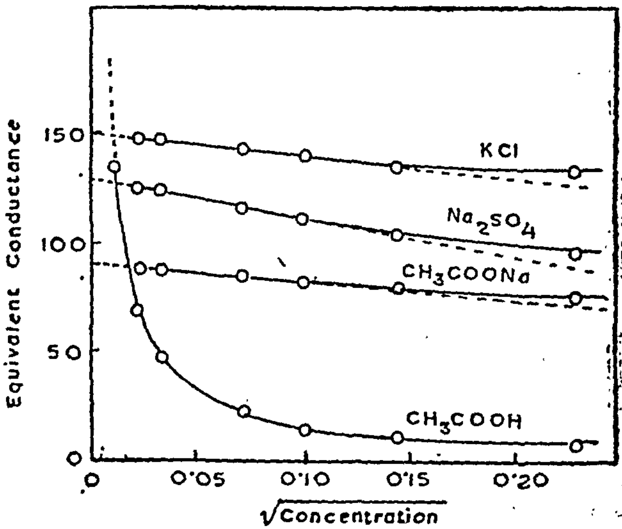


Fig. 5·11. Equivalent Conductance versus Square root of Concentration for some Electrolytes.

like KCl, Na_2SO_4 and CH_3COONa are linear particularly at low concentration, while that for weak electrolyte like CH_3COOH is non-linear. Thus, we can say that the electrolytes which give essentially linear plots are classed as **strong electrolytes**, while those which give non-linear plots are known as **weak electrolytes.**

In case of a strong electrolyte, the limiting value of its equivalent conductance can be obtained by extrapolting the plot to zero concentration as shown by dotted line in the figure. It should be noted that in case of weak electrolytes, this extrapolation method cannot be applied as is evident from the curve for a cetic acid. The curve is approaching almost tangentially to zero concentration.

Kohlrausch's Law

Since the method given above involving the extrapolation of Λ vs. $\sqrt{c}$ to zero concentration is not applicable for the evaluation of Λ_0 for weak electrolytes, it is determined by the application of **Kohlrausch's law of independent migration of ions.** Kohlrausch investigated the equivalent conductance at infinite dilution of a number of pairs of electrolytes having a common cation or anion at constant temperature. Some of the results at 25°C are shown in Table 5.4.

Table 5.4

Equivalent Conductances at Infinite Dilution of Various Pairs of Electrolytes at 25°C.

($ohm^{-1}\ cm^2\ equiv^{-1}$)

Pairs of Electrolytes with common anions	Λ_0	*Difference*	*Pairs of Electrolytes with common cations*	Λ_0	*Difference*
KCl	149·86	23·41	LiCl	115·03	4·90
NaCl	126·45		$LiNO_3$	110·13	
KNO_3	144·96	23·41	KCl	149·86	4·90
$NaNO_3$	121·55		KNO_3	144·96	
KOH	271·52	23·41	HCl	426·16	4·90
NaOH	248·11		HNO_3	421·26	

From the table it is evident that the difference in the equivalent conductance at infinite dilution of electrolytes having a common ion is constant at a particular temperature. For example, the difference between Λ_0 for electrolytes having Na^+ and K^+ ions with a common anion is 23·41. Similarly, the difference between Λ_0 for electrolytes having Cl^- and NO_3^- ions with a common cation is 4·90. The constancy in the difference of Λ_0 is possible only if each ion in an electrolyte makes a definite contribution towards the equivalent conductance of the solution irrespective of the other ion with

it is associated. Kohlrausch explained this on the basis that at infinite dilution the electrolyte is completely dissociated and all interionic effects disappear. Hence each ion moves independent of its co-ion. Each ion thus contributes its share to the total equivalent conductance of the electrolyte which depends on its nature only and not on the nature of its co-ion. This led Kohlrausch to enunciate the law known after his name as **Kohlrausch's law of the independent migration of ions.** The law states that *the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of equivalent ionic conductances of its cation and anion.* Thus,

$$\Lambda_0=\lambda_0^{+}+\lambda_0^{-} \qquad \text{...(5·41)}$$

where λ_0^+ and λ_0^- are the equivalent ionic conductances of cation and anion respectively at infinite dilution.

Determination of Equivalent Ionic Conductances from Transport Number. The values of equivalent ionic conductances can be obtained from their transport numbers at infinite dilution. The conductance depends upon the total charge carried by the ions and their speeds. We know that the ionization is complete at infinite dilution and the net charge carried by cations and anions is constant, hence the equivalent conductance at infinite dilution is dependent only on the speeds of the ions. It follows that the equivalent ionic conductances of cations and anions will be proportional to their speeds u^- and u^+ respectively. Thus,

$$\lambda_0^+ \propto u_+$$

or $$\lambda_0^+=ku_+ \qquad \text{...(5·42)}$$

and $$\lambda_0^- \propto u_-$$

or $$\lambda_0^-=ku_- \qquad \text{...(5·43)}$$

From Kohlrausch's law, the equivalent conductance at infinite dilution, Λ_0 is given by

$$\Lambda_0=\lambda_0^{+}+\lambda_0^{-}$$
$$=ku_++ku_-$$

or $$\Lambda_0=k(u_++u_-) \qquad \text{...(5.44)}$$

Dividing Eq. (5·42) by Eq. (5.44), we get

$$\frac{\lambda_0^+}{\Lambda_0}=\frac{ku_+}{k(u_++u_-)}=\frac{u_+}{u_++u_-}=t^0{}_+$$

or $$\lambda^{0+}=t^0{}_+\Lambda_0 \qquad \text{...(5·45)}$$

Similarly $$\lambda_0^-=t^0{}_-\Lambda_0 \qquad \text{...(5.46)}$$

where $t_+{}^0$ and $t_-{}^0$ are the transport numbers of cations and anions at infinite dilution respectively. These may be obtained by measuring the transport number at low concentrations and then extrapolating the plot t vs. c to zero concentration. Thus, knowing the value

of transport number of an ion and the total equivalent conductance at infinite dilution, the equivalent ionic conductance of the ion can be calculated. Equivalent ionic conductances of some of the ions, calculated from the best available values of Λ_0 and t^0, at 25°C have been summarized in Table 5·5.

Table 5.5

Equivalent Ionic Conductances at Infinite Dilution at 25°C.

($ohm^{-1}\ cm^2\ equiv^{-1}$)

Cations	λ_0^+	*Anions*	λ_0^-
H^+	349.82	Cl^-	76·34
Li^+	38·69	Br^-	78·40
Na^+	50·11	I^-	76·80
K^+	73·52	NO_3^-	71·44
NH_4^+	73·40	OH^-	198·00
Ag^+	61·92	CH_3COO^-	40·90
$\frac{1}{2}\ Ca^{++}$	59·50	HCO_3^-	44·48
$\frac{1}{2}\ Ba^{++}$	63·64	$\frac{1}{2}SO_4^{--}$	79·80
$\frac{1}{2}\ Sr^{++}$	59·46	ClO_4^-	68.00
$\frac{1}{3}\ La^{+++}$	69·6	$\frac{1}{4}\ Fe(CN)_6^{----}$	110·50

Example 10. *The transport numbers of Na^+ and Cl^- ions at infinite dilution are 0·3962 and 0.6038 respectively. If the equivalent conductance of sodium chloride solution at infinite dilution is 126·45 $ohm^{-1}\ cm^2\ equiv^{-1}$, calculate the equivalent ionic conductances of Na^+ and Cl^- ions at infinite dilution.*

Solution. We know that

$$\lambda_0^+ = t_+^\circ \times \Lambda_0$$

and $\lambda_0^- = t_-^\circ \times \Lambda_0$

Here $\Lambda_0 = 126{\cdot}45\ ohm^{-1}\ cm^2\ equiv^{-1}$

$$t_+^\circ = 0{\cdot}3962$$

$$t_-^\circ = 0{\cdot}6038$$

$$\therefore \lambda_0^+ = 0{\cdot}3962 \times 126{\cdot}45 = 50{\cdot}098\ ohm^{-1}\ cm^2\ equiv^{-1}$$

$$\lambda_0^- = 0{\cdot}6038 \times 126{\cdot}45 = 76{\cdot}361\ ohm^{-1}\ cm^2\ equiv^{-1}$$

$\therefore$ The equivalent ionic conductances at infinite dilution of Na^+ and Cl^- ions are 50.098 and 76·361 $ohm^{-}\ cm^2\ equiv^{-1}$ respectively.

Application of Kohlrausch's Law in the Determination of Equivalent Conductance of Weak Electrolytes at Infinite Dilution.

It has already been mentioned that the equivalent cond[illegible] of weak electrolyte at infinite dilution cannot be determined [illegible] However, such determination can be made indirectly with [illegible] Kohlrausch's law. There are two methods by which [illegible] electrolytes can be evaluated :

(*i*) **First Method.** This method is based on the fact that Λ_0 for strong electrolytes can be determined directly. To understand this method, let us take an example of the determination, of Λ_0 acetic acid. In this case, Λ_0 cannot be determined directly, but for NaCl, CH_3 COONa, and HCl can be obtained directly because all of them are strong electrolytes. These values are determined and Λ_0 for acetic acid can be evaluated in the following way :-

According to the Kohlrausch's law,

$$\Lambda_0 CH_3COONa = \lambda_0 Na^+ + \lambda_0 CH_3COO^- \quad ...(5{\cdot}47)$$

$$\Lambda_0 HCl = \lambda_0 H^+ + \lambda_0 Cl^- \quad ...(5{\cdot}48)$$

$$\Lambda_0 NaCl = \lambda_0 Na^+ + \lambda_0 Cl^- \quad ...(5.49)$$

and

$$\Lambda_0 CH_3COOH = \lambda_0 H^+ + \lambda_0 CH_3COO^- \quad ...(5{\cdot}50)$$

Adding Eqs. (5.47) and (5.48) and from this subtracting Eq. (5.49), we get

$$\begin{aligned}\Lambda_0 CH_3COONa + \Lambda_0 HCl - \Lambda_0 NaCl &= \lambda_0 Na^+ + \lambda_0 CH_3COO^- + \lambda_0 H^+ + \lambda_0 Cl^- - \lambda_0 Na^+ - \lambda_0 Cl^- \\ &= \lambda_0 H^+ + \lambda_0 CH_3COO^- \\ &= \Lambda_0 CH_3COOH \quad ...(5{\cdot}51)\end{aligned}$$

Thus, knowing the values of Λ_0 for CH_3COONa, HCl, and NaCl, Λ_0 for CH_3COOH can be evaluated.

Similarly, Λ_0 for NH_4OH can be obtained from the values of Λ_0 for NH_4Cl, NaOH, and NaCl by the following relation :

$$\Lambda_0 NH_4OH = \Lambda_0 NH_4Cl + \Lambda_0 NaOH - \Lambda_0 NaCl \quad ...(5{\cdot}52)$$

Example 11. *At 25°C, the equivalent conductance at infinite dilution of ammonium chloride, sodium hydroxide, and sodium chloride are 149·7, 248·11, and 126.45 ohm^{-1} cm^2 $equiv^{-1}$ respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution at 25°C.*

Solution. We know that

$$\Lambda_0 NH_4OH = \Lambda_0 NH_4Cl + \Lambda_0 NaOH - \Lambda_0 NaCl$$

$$\Lambda_0 NH_4Cl = 149{\cdot}70 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\Lambda_0 NaOH = 248{\cdot}11 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\Lambda_0 NaCl = 126{\cdot}45 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\therefore \quad \Lambda_0 NH_4OH = 149{\cdot}70 + 248{\cdot}11 - 126{\cdot}45$$

$$= 271{\cdot}36 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

(*ii*) **Second Method.** In this method, the equivalent ionic conductances, as determined from their transport numbers, are obtained for the cation and anion comprising the weak electrolyte. According to Kohlrausch's law, the sum of these two terms will give the equivalent conductance of the weak electrolyte at infinite dilution.

Example 12. *At 25°C, the equivalent conductances at infinite dilution of HCl and CH_3COONa are 426·16 and 91·0 ohm^{-1} cm^2 $equiv^{-1}$. If the transport numbers of H^+ and CH_3COO^- ions in these electrolytes are 0·821 and 0·449 respectively, calculate the equivalent conductance at infinite dilution of acetic acid.*

Solution. We know that

$$\lambda_o H^+ = t^o{}_+ \times \Lambda_o HCl$$

and $\lambda_o CH_3COO^- = t^o{}_- \times \Lambda_o CH_3COOH^-$

Here $t^o{}_+ = 0{\cdot}821$

$t^o{}_- = 0{\cdot}449$

$\Lambda_o HCl = 456{\cdot}19$ ohm^{-1} cm^2 $equiv^{-1}$

$\Lambda_o CH_3COONa = 91{\cdot}0$ ohm^{-1} cm^2 $equiv^{-1}$

$\therefore\ \lambda_o H^+ = 0{\cdot}821 \times 426{\cdot}19 = 349{\cdot}79$

$\lambda_o CH_3COO^- = 0{\cdot}449 \times 91{\cdot}0 = 40{\cdot}85$

Since $\Lambda_o CH_3COOH = \lambda_o H^+ + \lambda_o CH_3COO^-$

$\therefore\ \Lambda_o CH_3COO^- = 349{\cdot}79 + 40{\cdot}85$

$= 390{\cdot}64$ ohm^{-1} cm^2 $equiv^{-1}$

Ionic Mobilities

The actual speed of an ion in solution is directly proportional to the applied potential and inversely to the distance between the electrodes. In other words, the speed of an ion depends upon the potential gradient. *The speed of an ion in cm per sec under the potential gradient of 1 volt cm^{-1} is known as its* **ionic mobility.** It is represented by μ and has the units cm sec^{-1}/volt cm^{-1} or cm^{+2} sec^{-1} $volt^{-1}$. The equivalent ionic conductance at infinite dilution is proportional to the speed of that ion and hence also proportional to its ionic mobility. The relation between the two is given by

$$\lambda_o{}^+ = \mu^o{}_+ \times \mathcal{F} \qquad ...(5{\cdot}53)$$

$$\text{and } \lambda_o{}^- = \mu^o{}_- \times \mathcal{F} \qquad ...(5{\cdot}54)$$

$$\therefore\ \Lambda_o = \lambda_o{}^+ + \lambda_o{}^- = (\mu^o{}_+ + \mu^o{}_-) \times \mathcal{F} \qquad ...(5{\cdot}55)$$

where $\mathcal{F}$ is faraday equal to 96500 coulombs.

Thus, ionic mobilities of cations and anions are given as

$$\mu^o{}_+ = \frac{\lambda_o{}^+}{\mathcal{F}} \qquad ...(5{\cdot}56)$$

$$\mu^o{}_- = \frac{\lambda_o{}^-}{\mathcal{F}} \qquad ...(5{\cdot}57)$$

The ionic mobility can be obtained by dividing equivalent ionic conductance of the ion by the value of the faraday, *i.e.*, 96500 coulombs. Ionic mobilities of some ions, calculated in this way, are given in Table 5·6.

Table 5·6
Ionic Mobilities at Infinite Dilution at 25°C
(cm^2 sec^{-1} $volt^{-1}$)

Cations	μ_+ (*cm sec*$^{-1}$)	*Anions*	μ_- (*cm sec*$^{-1}$)
H^+	$36{\cdot}20\times10^{-4}$	Cl^-	$7{\cdot}91\times10^{-4}$
Li^+	$3{\cdot}88\times10^{-4}$	Br^-	$8{\cdot}12\times10^{-4}$
Na^+	$5{\cdot}20\times10^{-4}$	I^-	$7{\cdot}96\times10^{-4}$
K^+	$7{\cdot}62\times10^{-4}$	NO_3^-	$7{\cdot}40\times10^{-4}$
NH_4^+	$7{\cdot}60\times10^{-4}$	OH^-	$20{\cdot}50\times10^{-4}$
Ag^+	$6{\cdot}42\times10^{-4}$	CH_3COO^-	$4{\cdot}24\times10^{-4}$
Ca^{++}	$6{\cdot}16\times10^{-4}$	SO_4^{--}	$8{\cdot}27\times10^{-4}$

Example 13. *If the equivalent ionic conductance of NH_4^+ ion at infinite dilution is 73·40 ohm^{-1} cm^2 equiv^{-1} at 25°C. Calculate the ionic mobility of the ion at 25°C.*

Solution. We know that

$$\mu^\circ_+ = \frac{\lambda_0^+}{\mathcal{F}}$$

Here $\lambda_0^+ = 73{\cdot}40$ ohm^{-1} cm^2 equiv^{-1}

$\mathcal{F} = 96500$ coulombs

$$\therefore \quad \mu_0^+ = \frac{73{\cdot}40}{96500}$$

$$= 7{\cdot}607\times10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1},$$

Thus, the ionic mobility of NH_4^+ ion is $7{\cdot}607\times10^{-4}$ cm^2 sec^{-1} volt^{-1}.

Example 14. *If the ionic mobilities at infinite dilution of H^+ and CH_3COO^- ions at 25°C, are $36{\cdot}2\times10^{-4}$ and $4{\cdot}24\times10^{-4}$ cm^2 sec^{-1} volt^{-1} respectively, calculate the equivalent ionic conductances of each ion and the equivalent conductance at infinite dilution of acetic acid at 25°C.*

Solution. We know that

$$\lambda_0^+ = \mu^\circ_+ \times \mathcal{F}$$

and $$\lambda_0^- = \mu^\circ_- \times \mathcal{F}$$

Here $\mu^\circ_+ = 36{\cdot}2\times10^{-4}$ cm^2 sec^{-1} volt^{-1}

$\mu^\circ_- = 4{\cdot}24\times10^{-4}$ cm^2 sec^{-1} volt^{-1}

and $\mathcal{F} = 96500$ coulombs

$\therefore$ $\lambda_0^+ = 36{\cdot}2\times10^{-4}\times96500 = 349{\cdot}3$ ohm^{-1} cm^2 equiv^{-1}

$\lambda_0^- = 4{\cdot}24\times10^{-4}\times96500 = 40{\cdot}92$ ohm^{-1} cm^2 equiv^{-1}

Since $\Lambda_0 = \lambda_0^+ + \lambda_0^-$

$\therefore$ $\Lambda_0 = 349{\cdot}3 + 40{\cdot}92$

$= 390{\cdot}22$ ohm^{-1} cm^2 equiv^{-1}.

Variation of Ionic Conductance with Temperature

The equivalent ionic conductances at infinite dilution increase with the rise in temperature. This can be explained on the fact that

with the rise of temperature the viscosity of the solution decreases and hence the conductance increases. The variation of equivalent ionic conductance with temperature is given by the following empirical relation:

$$\lambda_o(t^\circ) = \lambda_o\,(25^\circ)\,[1+x(t-25)] \qquad ...(5{\cdot}58)$$

where $\lambda_o\,(t^\circ)$ and $\lambda_o\,(25^\circ)$ are the equivalent ionic conductances at t°C and 25°C respectively and x is a constant for each ion. For H^+ and OH^- ions the values of x are approximately 0·016 and 0·018 respectively and for other ions x may be taken equal to 0·02. With the help of this relation, the equivalent ionic conductances at infinite dilution at any temperature can be evaluated from the given values at 25°C.

Applications of Conductance Measurements.

There are a number of applications of conductance measurements. Some of the important ones will be discussed here.

(*i*) **Determination of Degree of Ionization of weak Electrolytes.** At infinite dilution the ionization of the electrolyte is complete and all ions formed from 1 gm equivalent of the electrolyte take part in conducting current. It has already been found that the equivalent conductance at infinite dilution is related to the ionic speeds by Eq. (5·44), *i.e.*,

$$\Lambda_o = k\,(u_+ + u_-) \qquad ...(5{\cdot}44)$$

At a particular concentration, the electrolyte is partially ionized. If α be the degree of ionization, then only a fraction α, of 1 gm equiv of ions takes part in conducting the current. Hence the equivalent conductance at a particular dilution, *i.e.*,

$$\Lambda = \alpha\,k\,(u_+ + u_-) \qquad ...(5{\cdot}59)$$

assuming that the velocities of ions do not change with dilution. Dividing Eq. (5·59) by Eq. (5·44), we get

$$\frac{\Lambda}{\Lambda_o} = \frac{\alpha\,k\,(u_+ + u_-)}{k\,(u_+ + u_-)} = \alpha \qquad ...(5{\cdot}60)$$

Eq. (5·60) shows that the degree of ionization can be found by measuring the conductances at particular and infinite dilutions. Actually, Eq. (5·60) gives a fairly good value of α for weak electrolytes, but it fails completely in case of strong electrolytes. This is explained on the basis that strong electrolytes are almost completely ionized even at moderate concentrations. This results in the mutual interaction of ions and the speeds of ions vary much with the change in concentration, which is contrary to the postulation in the deduction of Eq. (5·60). For this reason the quantity Λ/Λ_o is now termed as **conductance ratio** and not as degree of ionization. In case of

weak electrolytes, the number of ions is small. Hence the interionic attraction is also small and the speeds of ions do not vary much with change in concentration. Thus, $\Lambda/\Lambda_0 = \alpha$ holds true and the conductance ratio gives a fairly good value of α for weak electrolytes.

Example 15. *At 25°C, the equivalent conductance of 0·01 N ammonium hydroxide solution was found to be 11·3 ohm⁻¹ cm² equiv⁻¹. The equivalent ionic conductances at infinite dilution of NH_4^+ and OH^- ions at 25°C are 73·40 and 198·00 ohm⁻¹ cm² equiv⁻¹. Calculate the degree of dissociation of the base at this concentration.*

Solution. We know that

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Here

$$\Lambda = 11{\cdot}3 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- = 73{\cdot}40 + 198{\cdot}00$$

$$= 271{\cdot}40 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}.$$

$$\therefore \quad \alpha = \frac{11{\cdot}3}{271{\cdot}40} = 0{\cdot}04164$$

Thus, the degree of dissociation of 0·01 N NH_4OH = 0·04164.

(*ii*) **Determination of Solubilities of Sparingly Soluble Salts.** Although the salts like $BaSO_4$, $PbSO_4$, $AgCl$, etc., are regarded as insoluble salts, they do have some solubilities, however small they may be. The extremely small solubilities of these salts cannot be determined by ordinary chemical methods However, it has become possible to determine the solubility of such salts by conductance measurements.

The salt under investigation is washed and suspended in conductance water. It is then warmed and cooled again at 25°C. An extremely minute quantity of the salt will be dissolved and the rest will settle down. The specific conductance of the solution is determined as already described. Let it be κ_s. The specific conductance of conductivity water is also determined. Let it be κ_{H_2O}. The difference of the two, *i.e.* $(\kappa_s - \kappa_{H_2O})$ gives the specific conductance due to the ions of the dissolved salts. Since the value of κ_s is quite low, the correction for specific conductance of water is introduced. The solution is extremely dilute and hence it is assumed that all the electrolyte present in the dissolved state is completely ionized in its saturated solution. If the solubility of the salt is c gm equiv lit⁻¹, then its equivalent conductance would be $1000 \times (\kappa_s - \kappa_{H_2O})/c$. The solution is so dilute that this equivalent conductance may be taken as the equivalent conductance at infinite dilution, Λ_0. Thus,

$$\Lambda_0 = \frac{1000 \times (\kappa_s - \kappa_{H_2O})}{c}$$

or

$$c = \frac{1000 \times (\kappa_s - \kappa_{H_2O})}{\Lambda_0} \text{ gm equiv lit}^{-1}$$

Since $\quad \Lambda_0 = \lambda_0^+ + \lambda_0^-$,

$$c = \frac{1000 \times (\kappa_s - \kappa_{H_2O})}{\lambda_0^+ + \lambda_0^-} \text{ gm equiv lit}^{-1} \qquad ...(5\cdot61)$$

The values of λ_0^+ and λ_0^- are found from tables and c is determined. The solubility in gm lit^{-1} is calculated by multiplying c by the equivalent weight of the salt.

Example 16. *At 25°C, the specific conductance of a saturated solution of barium sulphate is $4\cdot44 \times 10^{-6}$ ohm^{-1} cm^{-1}. The specific conductance of the water used for the preparation of solution is $1\cdot34 \times 10^{-6}$ ohm^{-1} cm^{-1}. If the equivalent ionic conductances of $\frac{1}{2}Ba^{++}$ and $\frac{1}{2}SO_4^{--}$ ions are 63·64 and 79·80 ohm^{-1} cm^{-2} equiv^{-1} respectively, calculate the solubility of barium sulphate in gm lit^{-1}. (Equivalent weight of barium sulphate = 116·7.*

Solution. We know that

$$c = \frac{1000 \times (\kappa_s - \kappa_{H_2O})}{\lambda_0^+ + \lambda_0^-}$$

Here

$$\kappa_s = 4\cdot44 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$
$$\kappa_{H_2O} = 1\cdot34 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$
$$\lambda_0^+ = 63\cdot64 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ equiv}^{-1}$$
$$\lambda_0^- = 79\cdot80 \text{ ohm}^{-1} \text{ cm2 equiv}^{-1}$$

$$\therefore \quad C = \frac{1000 \times (4\cdot44 - 1\cdot34) \times 10^{-6}}{(63\cdot64 + 79\cdot80)}$$
$$= \frac{1000 \times 3\cdot10 \times 10^{-6}}{143\cdot44}$$
$$= 2\cdot162 \times 10^{-5} \text{ gm equiv lit}^{-1}$$

The solubility in gm lit^{-1} = $c \times$ Equivalent weight

$$= 2\cdot162 \times 10^{-5} \times 116\cdot7$$
$$= 2\cdot523 \times 10^{-3} \text{ gm lit}^{-1}$$

(*iii*) **Determination of Degree of Hydrolysis and Hydrolysis Constant.** When a salt of a weak acid or weak base is dissolved water, hydrolysis occurs to form free acid and free base. *The fraction of the total salt hydrolysed is termed as the* **degree of hydrolysis.** It has been possible to determine degree of hydrolysis by conductance measurements.

Consider, for example, a solution of salt BA of weak base and strong acid in which the following equilibrium is established due to hydrolysis.

$$\underset{\text{(Unhydrolysed salt)}}{BA} + \underset{\text{Excess water)}}{H_2O} \rightleftharpoons \underset{\text{(Free base)}}{BOH} + \underset{\text{(Free acid)}}{HA} \qquad ...(5\cdot62)$$

If h is the degree of hydrolysis of the salt, then for every gm equiv of the salt, the number of gm equiv of the unhydrolysed salt, free base, and free acid will be $(1-h)$, h, and h respectively present in solution at equilibrium.

As the base BOH is weak, it may be considered as almost unionized and contributing little towards the conductance of solution. Hence the equivalent conductance Λ of the salt solution is due to the conductance of $(1-h)$ equiv of unhydrolysed salt and h equiv of free acid.

$$\therefore \qquad \Lambda = (1-h)\,\Lambda_{(BA)} + h\Lambda_{0(HA)} \qquad \ldots(5{\cdot}63)$$

or

$$h = \frac{\Lambda - \Lambda_{(BA)}}{\Lambda_{0(HA)} - \Lambda_{(BA)}} \qquad \ldots(5{\cdot}64)$$

where $\Lambda_{(BA)}$ is the equivalent conductance of unhydrolysed salt at the given dilution and $\Lambda_{0(HA)}$ is the equivalent conductance of the free acid HA at infinite dilution. As the acid is strong, it may be considered as completely ionized in dilute solution. Hence $\Lambda_{0(HA)}$ may be taken as the equivalent conductance of HA at infinite dilution. Thus, $\Lambda_{0(HA)}$ may be obtained by applying Kohlrausch's law.

$$\Lambda_{0(HA)} = \lambda_{0(H^+)} + \lambda_{0(A^-)}$$

The equivalent conductance Λ of the solution at the given dilution is determined usually by measuring its specific conductance. To obtain $\Lambda_{(BA)}$, excess of weak base BOH is added to the solution so that the equilibrium is suppressed towards left in Eq. (5·62) and the hydrolysis of the salt is suppressed so much that the equivalent conductance of the mixture may be taken as the equivalent conductance $\Lambda_{(BA)}$ of the unhydrolysed salt. Thus, knowing Λ, $\Lambda_{(HA)}$ and $\Lambda_{(BA)}$ the degree of hydrolysis is calculated. The h of a salt of weak acid and strong base may similarly, be given by

$$h = \frac{\Lambda - \Lambda_{(BA)}}{\Lambda_{0(BOH)} - \Lambda_{(BA)}} \qquad \ldots(5{\cdot}65)$$

The value of hydrolysis donstant K_h is then obtained from Ostwald dilution law (Chapter 6).

$$K_h = \frac{h^2}{(1-h)V} \qquad \ldots(5{\cdot}66)$$

where V is the volume of solution in litres containing 1 mole of the salt.

Example 17. *The equivalent conductance of 0·002 M solution of aniline hydrochloride is 136·7 ohm^{-1} cm^{-2} equiv^{-1} at 25°C. The equivalent conductance in presence of excess of aniline is 101·3 ohm^{-1} cm^{2} equiv^{-1}. The equivalent conductance of hydrochloric acid solution is 426·16 ohm^{-1} cm^{2} equiv^{-1}. Assuming that the equivalent conducance of pure aniline is negligible, calculate the degree of hydrolysis and hydrolysis constant of aniline hydrochloride.*

Solution. We know that

$$h = \frac{\Lambda - \Lambda_{(BA)}}{\Lambda_{0(HA)} - \Lambda_{(BA)}}$$

Here
$$\Lambda = 136{\cdot}7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$
$$\Lambda_{(BA)} = 101{\cdot}3 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiu}^{-1}$$
$$\Lambda_{0(HA)} = 426{\cdot}16 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\therefore \quad h = \frac{136{\cdot}7 - 101{\cdot}3}{426{\cdot}16 - 101{\cdot}3} = \frac{35{\cdot}4}{324{\cdot}86}$$
$$= 0{\cdot}109$$

Further, we know that

$$K_h = \frac{h^2}{(1-h)V}$$

Here
$$h = 0{\cdot}109$$
$$V = \frac{1}{0{\cdot}002} = 500 \text{ lit}$$

$$\therefore \quad = \frac{(0{\cdot}109)^2}{(1-0{\cdot}109) \times 500} = \frac{(0{\cdot}109)^2}{0{\cdot}891 \times 500}$$
$$= 2{\cdot}667 \times 10^{-5}$$

(iv) Determination of Dissociation Constants of Weak Acids and Weak Bases. Suppose α is the degree of dissociation of a weak acid HA at the concentration c moles lit^{-1}. The concentrations of dissociated species will be $c\alpha$ moles lit^{-1} and that of undissociated acid will be $(c - c\alpha)$ or $c(1-\alpha)$ moles lit^{-1}. Thus, the dissociation equilibrium and the equilibrium concentration can be written as

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

Applying the law of mass action, the dissociation constant K_a of the acid is given by

$$K_a = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)}$$

$$= \frac{c\alpha^2}{(1-\alpha)} \qquad ...(5{\cdot}67)$$

Similarly, if K_b is the dissociation constant of a weak base then

$$K_b = \frac{c\alpha^2}{(1-\alpha)} \qquad ...(5{\cdot}68)$$

Since the acid or base is weak, the degree of dissociation given by

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Substituting $\Lambda/\Lambda_\circ$ for α in Eq. (5·67), we get

$$K_a = \frac{c(\Lambda/\Lambda_\circ)^2}{(1-\Lambda/\Lambda_\circ)}$$

$$= \frac{\Lambda^2 c}{\Lambda_\circ(\Lambda_\circ-\Lambda)} \quad ...(5·69)$$

Similary

$$K_b = \frac{\Lambda^2 c}{\Lambda_\circ(\Lambda_\circ-\Lambda)} \quad ...(5·70)$$

$K_a = \frac{C\alpha^2}{(1-\alpha)}$

Example 18. *At 25°C, the equivalent conductance of 0·01 N acetic acid solution is 16·3 ohm^{-1} cm^2 equiv^{-1}. The equivalent ionic conductances at infinite dilution of H^+ and CH_3COO^- ions at 25°C are 349·82 and 40·90 ohm^{-1} cm^2 equiv^{-1} respectively. Calculate the dissociation constant of acetic acid.*

Solution. We know that

$$K_a = \frac{\Lambda^2 c}{\Lambda_\circ(\Lambda_\circ-\Lambda)}$$

Here Λ = 16·3 ohm^{-1} cm2 equiv^{-1}

c = 0·01 gm equiv lit^{-1}

$\Lambda_\circ = \lambda^+_\circ + \lambda^-_\circ = 349·82+40·90$

$= 390·72$

$\therefore \quad K_a = \frac{(16·32)\times 0·01}{390·72(390·72-16·3)}$

$= \frac{(16·3)^2\times 0·01}{390·72\times 374·42}$

$= 1·816\times 10^{-5}$

(v) Determination of Ionic Product of Water. It is known that water is slightly ionized and the following equilibrium exists :

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying the law of mass action, the equilibrium constant K is given by

$$K = \frac{[H^+][OH^-]}{[H_2O]} \quad ...(5·71)$$

As the concentration of unionized water molecules is in large excess, $[H_2O]$ may be taken as constant. Hence, we can write

$$K_w = [H^+][OH^-] \quad ...(5·72)$$

where K_w is another constant known as **ionic product** of water. The concentrations $[H^+]$ and $[OH^-]$ are expressed in moles lit^{-1}. The numerical value of K_w can be determined by the conductance measurements.

The specific conductance κ of perfectly pure water is foundto be $5{\cdot}54 \times 10^{-8}$ ohm^{-1} cm^{-1} at 25°C. Since the concentrations of H^+ and OH^+ ions existing in pure water are very small, the equivalent conductances of H^+ and OH^- ions may be taken to be equal to those at infinite dilution. The ionic conductances of H^+ and OH^- ions at infinite dilution are 349·8 and 198·6 ohm^{-1} cm^2 equiv^{-1} respectively. Thus, the equivalent conductance Λ of water may be written as

$$\Lambda = 349{\cdot}8 + 198{\cdot}6$$

$$= 548{\cdot}4 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

Now we know that

$$\Lambda = \frac{1000 \times \kappa}{c}$$

where c is the concentration of H^+ and OH^- ion in gm equiv lit^{-1}.

$$\therefore \qquad c = \frac{1000 \times \kappa}{\Lambda}$$

$$= \frac{1000 \times 5{\cdot}54 \times 10^{-8}}{548{\cdot}4}$$

$$= 1{\cdot}01 \times 10^{-7} \text{ gm equiv lit}^{-1}.$$

As the number of H^+ and OH^- ions are equal, the concentration of each of the H^+ and OH^- ions is $1{\cdot}01 \times 10^{-7}$ gm equiv lit^{-1}. Since the ions are univalent, gm equiv and gm ion (mole) are the same. Hence the concentration of each of the H^+ and OH^- ions $1{\cdot}01 \times 10^{-7}$ mole lit^{-7}. Putting these values in Eq. (5·72,) we get

$$K_w = (1{\cdot}01 \times 10^{-7})\ (1{\cdot}01 \times 10^{-7})$$

$$= 1{\cdot}02 \times 10^{-14}.$$

(vi) **Conductometric Titrations.** An important practical application of the conductance measurements is conductometric titrations, *i.e.*, determination of equivalence or end point of reactions between electrolytes. Conductometric titrations are based on the fact that during titrations ions of the titrant combine with ions of the titre to form weakly ionized molecules *e.g.*, $H^+ + OH^- = H_2O$ or a less soluble substance, *e g.*, $Ag^+ + Cl^- = AgCl$. The ions thus removed are replaced by equivalent amounts of other ions. Since the new ions have different conductances, such replacement causes a change in the conductance of the solution. The trend of change of conductance of the solution before and after the equivalence point are different The equivalence point is determined by graphical method.

Conductometric titrations are carried out by taking a known volume of one of the solutions in a suitable conductance cell. One of the cells, which is commonly used for titration purpose is shown in Fig. 5·12. The other *solution, which should be* about five times stronger than the solution in the cell, is added gradually from the burette. The conductance of the solution after each addition is measured using Wheatstone bridge. The observed conductance after each addition is corrected for the dilution effect by multiplying it with a factor $\frac{V+x}{V}$, where V refers to the volume of the solution taken initially in the cell and x is the volume of the titrant added. The corrected conductance is then plotted against the volume of the titrant added. Two straight or nearly straight lines, intersecting at a point, are obtained. The point of intersection gives the equivalence point of the titration. The volume corresponding to this point is noted from the graph and the strength of unknown solution is evaluated.

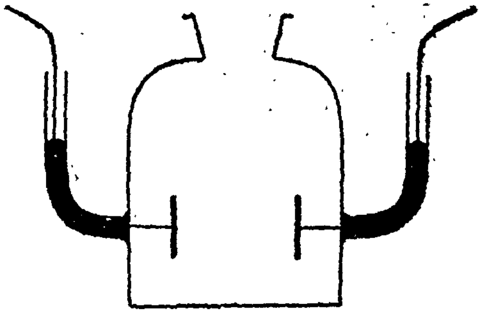


Fig. 5·12. Conductance cell for Titrations

Now we shall discuss two types of titrations : (*i*) Acid-base titrations and (*ii*) Precipitation titrations.

(*i*) Acid-Base Titration.

(*a*) *Titration of Strong acid with Base.* Suppose a *strong acid*, say hydrochloric acid, is titrated with a *strong base*, say sodium hydroxide. Since both are strong, they may be assumed to be completely dissociated in solution. The reaction may be represented as

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O \qquad ...(5·73)$$

The acid solution is taken in the conductance cell and the base in the burette. Initially, the conductance of hydrochloric acid solution is due to H^+ ions and Cl^- ions. When some sodium hydroxide solution is added, the fast moving H^+ ions are removed to form water and replaced by slow moving Na^+ ions as is evident from

Eq. (5·73). It follows that the conductivity of the solution decreases. On further addition of the base, the conductivity will further decrease. After the equivalence point no more H^+ ions are present. Further addition of base causes an increase in the conductance of the solution due to the addition of free OH^- ions. The plot I *in* Fig. 5·13 represents the result of such titration.

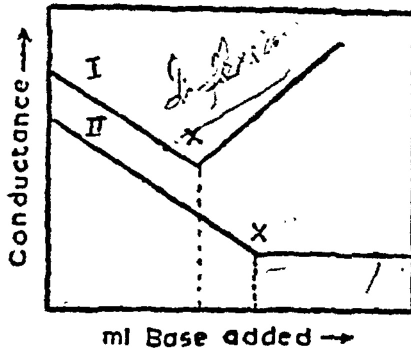


Fig. 5·13. Conductometric Titration curves.
I. Strong acid with strong base
II. *Strong acid with Weak base*
(*x* is the equivalence point)

In place of strong base sodium hydroxide suppose a weak base, say ammonium hydroxide is taken in the above case, the reaction may be represented by

$$H^+ + Cl^- + NH_4OH \rightarrow NH_4^+ + Cl^- + H_2O$$

When base is added to the acid, the fast moving H^+ ions are replaced by slow moving NH_4^+ *ions and hence the conductance of the solution* decreases. After equivalence point, further addition of ammonium hydroxide solution causes practically no change in the conductance of the solution because ammonium hydroxide is a weak base. This behaviour is shown by plot II in Fig. 5·13.

(*b*) *Titration of Weak Acid with Base.* When acid is weak and the base is strong, the titration curves will be of the type as shown by plot I in Fig. 5·14. Suppose acetic acid is titrated against sodium hydroxide, the reaction may be represented as

$$CH_3COOH + Na^+ + OH^- \rightarrow$$
$$CH_3COO^- + Na^+ + H_2O$$

Acetic acid being weak acid has a low conductance. When base is added, poorly conducting acid is converted into highly ionized sodium acetate nnd hence the conductivity of the solution increases. After the equivalence point, further addition of sodium hydroxide solution furnishes highly conducting free OH^- ions and hence the conductivity of the solution increases more sharply.

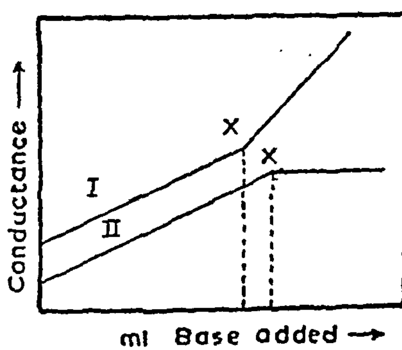


Fig. 5·14
Coductometric Titration Curves
I. Weak acid with Strong base
II. Weak acid with Weak base

If both the acid and the base are weak, then the titration curve will be of the type as shown by plot II in Fig. 5·14. Suppose acetic

acid is titrated against ammonium hydroxide, the reaction may be represented as

$$CH_3COOH + NH_4OH \longrightarrow CH_3COO^- + NH_4^+ + H_2O$$

Initially the conductance will be low because acetic acid is weak. The addition of ammonium hydroxide will result in the formation of highly conducting ammonium acetate and hence the conductivity of the solution increases. After equivalence point, the addition of ammonium hydroxide contributes very little to the conductance of the solution because the base is weak, and hence the conductance of the solution remains practically unchanged.

(*ii*) **Precipitation Titrations.** In case of precipitation titrations, *e.g.*, titration between silver nitrate and potassium chloride, the titration curve is shown in Fig. 5·15. The reaction may be represented as

$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow K^+ + NO_3^- + AgCl$$

Initially the conductance of silver nitrate solution is due to the Ag^+ and NO_3^- presents in the solution. The addition of potassium chloride involves the replacement of Ag^+ ions by K^+ ions. Since both these ions have almost same conductances, the conductance of the solution does not change appreciably. After equivalence point, the addition of potassium chloride furnishes more free Cl^- ions and hence the conductance of the solution increases.

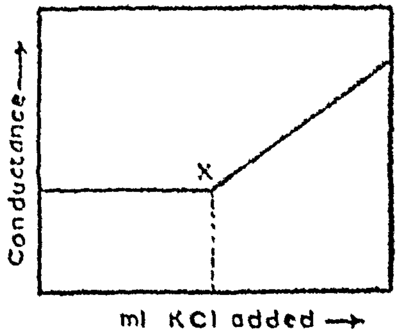


Fig. 5·15. Conductometric Titration Curves for silver nitrate with Potassium Chloride.

Advantages of Conductometric Titrations. The conductometric titrations have the following advantages :

(*i*) Dilute solutions can be titrated.

(*ii*) Coloured solutions, *e.g.*, dye stuffs, where ordinary indicators fail to determine the exact equivalence point, can be titrated.

(*iii*) Titration of weak acid with weak base can be carried out onductometrically.

(*iv*) Even mixtures of weak and strong acids *e.g.*, (acetic acid +hydrochloric acid) can be titrated.

(*v*) Since the equivalence point is determined graphically, only a few measurements before and after the equivalence point are enough and no extra care is to be taken at the equivalence point.

TEST YOUR KNOWLEDGE

1. Complete the following :

(i) $m = \dfrac{I \times t \times E}{\ldots\ldots\ldots}$

(ii) $t_+ = \dfrac{\ldots\ldots}{u_+ + u_-}$

(iii) $t_+ = \dfrac{N_I + N_E - N_F}{\ldots\ldots\ldots\ldots}$

(iv) $t_+ = \dfrac{l \times a \times c}{\ldots\ldots}$

(v) $L = \dfrac{a}{\ldots l}$

(vi) $\Lambda = \dfrac{1000\kappa}{\ldots\ldots}$

(vii) $\ldots = L\,K$

(viii) $K = \kappa \times \ldots\ldots$

(ix) $\ldots = \lambda_0^+ + \lambda_0^-$

(x) $\lambda_0^+ = t_+^0 \times \ldots\ldots$

(xi) $\lambda_0^+ = \mu^0_+ \times \ldots\ldots$

(xii) $\ldots. = (\mu^0_+ + \mu^0_-) \times \mathfrak{F}$

(xiii) $\ldots. = \Lambda / \Lambda_0$

(xiv) $c = \dfrac{3000\,(\kappa_s - \ldots)}{\lambda_0^+ + \lambda_0^-}$

(xv) $K\alpha = \dfrac{\ldots\ldots\ldots\ldots}{\Lambda_0(\Lambda_0 - \Lambda)}$

2. Give a term for each of the following :

(i) Substances which allow the current to pass through them.

(ii) Process of electrolytic conduction accompanying a chemical change in the electrolyte.

(iii) Quantity of electricity required to deposit 1 gm equivalent of a metal at cathode.

(iv) The fraction of the total current carried across by a particular type of ion.

(v) The reciprocal of resistance.

(vi) Conductance of a solution between two electrodes of 1 sq cm cross sectional area placed 1 cm apart.

(vii) The conductance due to all the ions produced by 1 gm equiv of the electrolyte in solution.

(viii) A factor which when multiplied with the conductance gives specific conductance of the solution.

(ix) The speed of ion in cm sec^{-1} under the potential gradient of 1 volt cm^{-1}.

(x) The fraction of the total salt hydrolysed.

3. **Fill in the blanks with appropriate words :**

(*i*) The charge carriers in electronic conductors are......and in electrolytic conductors are......

(*ii*) The ions are always discharged in.........amounts at the electrodes irrespective of their speeds.

(*iii*) The lesser the ion is hydrated the...........would be its transport number.

(*iv*) The reciprocal of the specific resistance is called the.........and has the units.........

(*v*) The units of equivalent conductance are..........

(*vi*) The specific conductance of a solution...........while the equivalent conductance.........with dilution.

(*vii*) For strong electrolytes, the plot of Λ vs. $\sqrt{c}$ at lower concentrations is.........

(*viii*) The equivalent conductance at infinite dilution of an electrolyte is equal to the sum of.........of its cation and anion.

(*ix*) The units of ionic mobility are.........

(*x*) The ratio Λ/Λ_0 gives the value of.........in case of weak electrolytes. In case of strong electrolytes it is called the.........

KEY

1. (*i*) $\mathfrak{F}$, (*ii*) u_+, (*iii*) N_E, (*iv*) $1000Q$, (*v*) κ, (*vi*) c, (*vii*) κ, (*viii*) R, (*ix*) Λ_0, (*x*) Λ_0, (*xi*) $\mathfrak{F}$, (*xii*) Λ_0, (*xiii*) a, (*xiv*) κ_{H_2O}, (*xv*) $\Lambda^2 c$.

2. (*i*) Conductors of electricity, (*ii*) Electrolysis, (*iii*) One faraday, (*iv*) Transport number of ion, (*v*) Conductance, (*vi*) Specific Conductance, (*vii*) Equivalent conductance, (*viii*) Cell constant, (*ix*) Ionic mobility, (*x*) Degree of hydrolysis.

3. (*i*) electrons, ions, (*ii*) equivalent, (*iii*) more, (*iv*) specific conductance, $ohm^{-1}\ cm^{-1}$, (*v*) $ohm^{-1}\ cm^2\ equiv^{-1}$, (*vi*) decreases, increases, (*vii*) linear, (*viii*) equivalent ionic conductances, (*ix*) $cm^2\ sec^{-1}$, $volt^{-1}$, (*x*) degree of dissociation, conductance ratio.

QUESTIONS

1. Explain the following terms with examples :
   (*i*) Conductors, (*ii*) Electrolytes, (*iii*) Electrolytic conductors, (*iv*) Electronic conductors and, (*v*) Non-electrolytes.
2. What is electrolysis ? Explain the mechanism of electrolysis.
3. State and explain Faraday's laws of electrolysis. Explain the terms coulomb, faraday, and electro-chemical equivalent.
4. How will you demonstrate the migration of ions ? Show with the help of examples that the loss of equivalents in any electrode compartment is proportional to the speed of ion leaving that compartment.
5. What is transport number of an ion ? Describe the Hittorf method for its determination.
6. Describe the moving boundary method for the determination of transport numbers.
7. Explain specific conductance, equivalent conductance, and molar conductance. What is the relation between them ? Mention the effect of dilution on them.

8 How will you determine experimentally the conductance and specific conductance of an electrolyte ?

9. State and explain the Kohlrausch law. How this law helps in the determination of the equivalent conductance at infinite dilution of a weak electrolyte. How are equivalent ionic conductances related with transport numbers ?

10. Give the various applications of conductance measurements.

11. What is the principle of conductometric titrations ? Give its advantages. Discuss the conductometric titrations in the following cases.

(*i*) Strong acid with strong base and weak base.

(*ii*) Weak acid with strong base and weak base.

(*iii*) Precipitation reactions.

12. Write short notes on the following :

(*i*) Conductance cells

(*ii*) Ionic mobility

(*iii*) Coulometers

(*iv*) Conductometric titrations.

13. Explain why ?

(*i*) In the electrolysis of aqueous NaOH solution, H_2 gas is evolved at cathode and Na is not deposited.

(*ii*) One gm equivalent of every substance is deposited by one faraday.

(*iii*) *In the determination of conductance of an electrolyte,* A.C. is used in place of D.C.

(*iv*) The specific conductance of an electrolyte decreases and equivalent conductance increases with dilution.

(*v*) The conductance ratio Λ/Λ_0 gives the degree of dissociation for weak electrolytes, but not for strong electrolytes.

14. In an electrolysis of alumina in molten cryolite, 20 amp current was passed for 75 min. Calculate the amount of aluminium deposited on the cathode. Also calculate how many litres of oxygen gas is liberated at N.T.P. (Equivalent weight of Aluminium is 8·997)

[Ans. 8·392 gm, 5·224 lit]

5. A solution of silver nitrate containing 0·0074 gm of $AgNO_3$ per gm of water was electrolysed in Hittorf apparatus between silver electrodes. The anode solution after electrolysis which was weighed equal to 23·378 gms contained 0·238 gm of $AgNO_3$. In a silver coulometer in series 0·07798 gm of silver was deposited. Calculate the transport numbers of Ag^+ and NO_3^- ions. (Eq. weight of Ag = 107·87 and $AgNO_3$ = 169·87)

[Ans. t_+ = 0·4563, t_- = 0·5437]

6. In electrolysis of copper sulphate solution between copper electrodes the total mass of copper deposited on the cathode was 0·254 gm and the masses of copper sulphate before and after electrolysis were 1·500 gm and 2·125 gm respectively. Calculate the transport numbers of Cu^{++} and SO_4^{--} ions. (Copper = 63·54 copper sulphate = 249·54)

[Ans. t_+ = 0·3733, t_- = 0·6267]

7. Silver nitrate solution was electrolysed between platinum electrodes. The concentration of silver nitrate in both the compartments before electrolysis was 10·075 gm and after electrolysis it was 9·420 and 9·305 gm in the anode and cathode compartments respectively. Calculate the transport numbers of Ag^+ and NO_3^- ions.

[Ans. t_+ = 0·4801, t_- = 0·5199]

18. In a moving boundary experiment for the determination of transport number of ions in 0·01N NaCl using $CdCl_2$ solution as the indicator solution at 25°C, it was observed that with the current of 0·0032 amp, the time required to move the boundary through 4·0 cm was 1330 sec. The area of cross section of the tube was 0·1113 cm². Calculate the transport number of Na^+ and Cl^- ions.

[Ans. $t_+ = 0·3892$, $t_- = 0·6108$]

19. A conductance cell containing a solution of 0·01 N KCl at 18°C offered a resistance of 200 ohms. If the specific conductance of 0·01 N KCl solution at 18°C is 0·001223 cm^{-1}, calculate the cell constant.

[Ans. 0·2446 cm^{-1}]

20. 0·5 N solution of a salt occupying a volume between two platinum electrodes 1·72 cm apart and of area 4·5 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.

[Ans. 30·58 ohm^{-1} cm^2 $equiv^{-1}$]

21. A conductivity cell containing 0·1 M KCl solution at 25°C offered a resistance of 18·9 ohms. If the cell constant of the cell is 0·2438 cm^{-1}, calculate (*a*) the specific conductance and (*b*) the equivalent conductance of the solution.

[Ans. (*a*) 0·01290 ohm^{-1} cm^{-1} (*b*) 129·0 ohm^{-1} cm^2 $equiv^{-1}$]

22. The transport numbers of Ag^+ and NO_3^- ions at infinite dilution at 25°C are 0·4641 and 0·5359 respectively. If the equivalent conductance at infinite dilution of silver nitrate solution is 133·36 ohm^{-1} cm^2 $equiv^{-1}$, calculate the equivalent ionic conductances of Ag^+ and NO_3^- ions at infinite dilution.

[Ans. $\lambda_0^+ = 61·90$ ohm^{-1} cm^2 $equiv^{-1}$, $\lambda_0^- = 71·48$ ohm^{-} cm^2 $equiv^{-1}$]

23. At 25°C, the equivalent conductances at infinite dilution of sodium acetate, hydrochloric acid, and sodium chloride are 91·01, 426·16, and 126·45 ohm^{-1} cm^{-2} $equiv^{-1}$. Calculate the equivalent conductance of acetic acid at infinite dilution at 25°C.

[Ans. 390·72 ohm^{-1} cm^2 $equiv^{-1}$]

24. At 25°C the equivalent conductances at infinite dilution of NH_4Cl and NaOH are 149·74 and 248·11 ohm^{-1} cm^2 $equiv^{-1}$. If the transport numbers of NH_4^+ and OH^- ions in these electrolytes are 0·4903 and 0·798 respectively, calculate the equivalent conductance at infinite dilute of ammonium hydroxide.

[Ans. 271·91 ohm^{-1} cm^2 $equiv^{-1}$]

25. If the equivalent ionic conductance of CH_3COO^- ion at infinite dilution is 40·90 ohm^{-1} cm^2 $equiv^{-1}$ at 25°C. Calculate the ionic mobility of the ion at 25°C.

[Ans. $4·238 \times 10^{-4}$ cm^2 sec^{-1} $volt^{-1}$]

26. If the ionic mobilities at infinite dilution of NH_4^+ and OH^- ions at 25°C are $7·60 \times 10^{-4}$ and $20·50 \times 10^{-4}$ cm^2 sec^{-1} $volt^{-1}$ respectively, calculate the equivalent conductance at infinite dilution of ammonium hydroxide at 25°C.

[Ans. 271·1 ohm^{-1} cm^2 $equiv^{-1}$]

27. At 25°C, the specific conductance of 0·1 N acetic acid solution is 0·0005274 ohm^{-1} cm^{-1}. If the equivalent ionic conductances at infinite dilution of H^+ and CH_3COO^- ions are 349·82 and 40·90 ohm^{-1} cm^2 $equiv^{-1}$ respectively at 25°C. Calculate the degree of dissociation of the acid.

[Ans. 0·0135]

28. The specific conductance of a saturated solution of AgCl at 25°C was found to be $3{\cdot}41 \times 10^{-6}$ ohm^{-1} cm^{-1}. The specific conductance for water used to make up the solution was $1{\cdot}60 \times 10^{-6}$ ohm^{-1} cm^{-1}. Determine the solubility of AgCl in water in moles lit^{-1} at 25°C. The equivalent conductance of AgCl at infinite dilution is 138·3 ohm^{-1} cm^{2} equiv^{-1}. (Eq. weight of AgCl is 143·32)

[Ans. $1{\cdot}876 \times 10^{-5}$ moles lit^{-1}]

29. At 25°C, the equivalent conductance of a solution of aniline hydrochloride was found to be 150 ohm^{-1} cm^{2} equiv^{-1} at certain dilution. In presence of excess of aniline the value of equivalent conductance was found to be 100 ohm^{-1} cm^{2} equiv^{-1}. If the equivalent conductance at infinite dilution of HCl at 25°C is 426·16 ohm^{-1} cm^{2} equiv^{-1}, calculate the degree of hydrolysis of the salt.

[Ans. 15·33%]

30. At 25°C, the equivalent conductance of 0·05 N acetic acid solution was found to be 7·358 ohm^{-1} cm^{-1}. The equivalent ionic conductances at infinite dilution of H^+ and CH_3COO^- ions at 25°C are 349·82 and 40·90 ohm^{-1} cm^{2} equiv^{-1} respectively. Calculate the dissociation constant of acetic acid.

[Ans. $1{\cdot}807 \times 10^{-5}$]

6

Ionic Equilibria

Introduction

The conductance of the aqueous solutions of electrolytes and their electrolysis have already been studied in the last chapter. Faraday studied the phenomena associated with electrolysis of electrolytes in 1832. Kohlrausch published a long series of papers on the conductance of electrolytes from 1869 to 1880. At this stage, the study of colligative properties of dilute solutions by van't Hoff revealed that large deviations are found from the van't Hoff equation in case of electrolytes. Thus, one of the fundamental theoretical problems in physical chemistry was to explain such peculiar behaviour of electrolytes. Some attempts were made by Grotthus and Clausius but they could not give a satisfactory mechanism to explain the electrolytic conduction and the various related phenomena. Arrhenius in 1887 gave a satisfactory theory of electrolytic dissociation which not only explained these behaviour of electrolytes, but in fact, formed the basis of modern treatment of electrolytes.

Arrhenius Theory of Electrolytic Dissociation

When Arrhenius proposed the theory of electrolytic dissociation, electron was not discovered and very little was known about the structure of atom. Hence Arrhenius theory has been modified in the light of modern discoveries. The theory, in its modern form, consists of the following postulates :

(*i*) When electrolytes are dissolved in water, they dissociate spontaneously into positively and negatively charged particles called **ions.** The positively charged particles are called **cations** and the negatively charged particles are called **anions.** The ions are free to move in the solution.

(*ii*) The ions in the solution are constantly recombining to form the undissociated molecules and hence a dynamic equilibrium exists between the dissociated and the undissociated molecules.

$$AB \rightleftharpoons A^+ + B^- \qquad \ldots(6{\cdot}1)$$

Such an equilibrium is called **ionic** or **dissociation equilibrium.**

(*iii*) The fraction of the electrolyte dissociated is called the **degree of dissociation.** The degree of dissociation increases with

dilution. Its value tends to approach unity at infinite dilution when the electrolyte is regarded as completely dissociated into ions.

(*iv*) The total positive charge of all the cations is equal to the total negative charge of all the anions present in the solution and hence the solution as such is neutral.

(*v*) When a potential is applied to the solution, cations move towards the cathode and anions towards the anode. This movement of ions is responsible for the conduction of the electric current in solution. The conductance depends upon the number and nature of ions.

(*vi*) Each ion behaves like a molecule in displaying the colligative properties like osmotic pressure, freezing point lowering, boiling point elevation, etc., of the solutions.

(*vii*) The properties of an electrolytic solution are the properties of its ions.

These postulates led Arrhenius to calculate the degree of dissociation of electrolytes from conductance measurements. He argued that the increase in the equivalent conductance of an electrolyte with dilution is due to the increase in the degree of dissociation. At infinite dilution, the electrolyte is completely dissociated. Hence the degree of dissociation approaches the maximum value i.e., unity and consequently equivalent conductance also reaches its maximum value. Thus, the ratio of equivalent conductance of an electrolyte at any particular dilution and that at infinite dilution should give the degree of dissociation α of the electrolyte at that dilution. Hence, Arrhenius gave the relation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \qquad \ldots(6\cdot2)$$

where Λ and Λ_∞ are the equivalent conductances of an electrolyte at a particular dilution and at infinite dilution respectively. Thus, he could calculate degree of dissociations of various electrolytes at different dilutions. van't Hoff also calculated the degree of dissociations of electrolytes by studying their colligative properties using the relation

$$\alpha = \frac{i-1}{\nu-1} \qquad \ldots(6\cdot3)$$

where i is the van't Hoff factor and ν is the number of ions into which the electrolyte splits up. It was found that the values of degree of dissociations calculated by Eq. (6·2) tallied fairly well with those calculated by Eq. (6·3). Thus, the theory of Arrhenius got strong support.

Further, a strong evidence in favour of [illegible] furnished by Ostwald (1888) by deducing the [illegible]

Ostwald's Dilution Law

Ostwald applied the law of mass action to the ionic equilibria postulated by Arrhenius and derived a relation governing the variation of equivalent conductance of the electrolyte and its concentration. Let us take a general electrolyte A_xB_y which on dissociation gives x ions of A each having charge z_+ and y ions of B each having charge z_- according to the equation

$$A_xB_y \rightleftharpoons xA^{z+} + yB^{z-} \qquad \ldots(6\cdot4)$$

Suppose the original concentration of the electrolyte is c moles lit^{-1} and the degree of dissociation is α. The initial and the equilibrium concentrations of the various species in the solution are given as

	$A_xB_y \rightleftharpoons$	$xA^{z+}+$	yB^{z-}
Initial conc.	c	0	0
Equilibrium conc.	$c(1-\alpha)$	$xc\alpha$	$yc\alpha$

Applying the law of mass action, the equilibrium constant expression is

$$K = \frac{[A^{z+}]^x\,[B^{z-}]^y}{[A_xB_y]}$$

$$= \frac{(xc\alpha)^x\,(yc\alpha)^y}{c(1-\alpha)}$$

or

$$K = \frac{x^x\,y^y\,(\alpha^{x+y})\,c^{(x+y-1)}}{(1-\alpha)} \qquad \ldots(6\cdot5)$$

This is general mathematical form of **Ostwald's dilution law.** K is known as **dissociation constant** or **ionization constant.**

In case of dissociation of uni-univalent electrolyte according to the equation

	$AB \rightleftharpoons$	$A^+ +$	B^-
Initial conc	c	0	0
Equilibrium conc	$c(1-\alpha)$	$c\alpha$	$c\alpha$

where $x = y = 1$, Eq. (6·5) reduces to

$$K = \frac{c\alpha^2}{1-\alpha} \qquad \ldots(6\cdot6)$$

For an electrolyte of the type AB_2, the dissociation is given by

	$AB_2 \rightleftharpoons$	$A^{2+} +$	$2B^-$
Initial conc.	c	0	0
Equilibrium conc.	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Here $x = 1$, $y = 2$ and hence Eq. (6·5) reduces to

$$K = \frac{4c^2\alpha^3}{1-\alpha} \qquad \ldots(6\cdot7)$$

For simplicity we take the case of uni-univalent electrolyte. Putting the value of α from the Arrhenius expression $\alpha=\Lambda/\Lambda_0$ in Eq. (6·6) we get,

$$K=\frac{c(\Lambda/\Lambda_0)^2}{1-(\Lambda/\Lambda_0)}$$

or $$K=\frac{c\Lambda^2}{\Lambda_0(\Lambda_0-\Lambda)} \qquad ...(6·8)$$

This is mathematical expression of Ostwald's dilution law as applied to the *uni univalent electrolyte.*

For uni-univalent *weak electrolytes*, α is very small as compared to 1. Hence in eq. (6·6), $(1-\alpha)$ may be taken equal to 1. Eq. (6·6) takes the form.

$$K=c\alpha^2$$

or $$\alpha=\sqrt{K/c} \qquad ...(6·9)$$

This is an approximate form of Ostwald's dilution law for uni-univalent weak electrolytes.

It can be seen from Eq. (6·5) that as $c\rightarrow 0$, α must increase and tends to unity to maintain the constant value of K. Thus, the fact that the degree of dissociation increases with dilution is essentially a consequence of the existence of a dissociation equilibrium postulated by Arrhenius in which the number of particles increases due to dissociation.

Verification of Ostwald's Dilution Law. In order to verify the Ostwald dilution law experimentally, equivalentc onductance, Λ, of an electrolyte are determined at various concentrations c. The value of equivalent conductance at infinite dilution Λ_0 can be obtained by Kohlraush law

$$\Lambda_0=\lambda^+{}_0+\lambda^-{}_0$$

where λ_0^+ and λ_0^- are equivalent ionic conductances at infinite dilution of cations and anions respectively consisting the electrolyte. The values of $\lambda^+{}_0$ and $\lambda^-{}_0$ are found from the tables. The values of Λ, c and Λ_0 are then put in the following equation

$$K=\frac{c\Lambda^2}{\Lambda_0(\Lambda_0-\Lambda)}$$

and the value of K is determined at various dilutions. *It is found that the value of K comes out to be reasonably constant in case of weak electrolytes at a given temperature. Table 6·1 shows the values of K of acetic acid at various dilutions at 25°C.*

Table 6·1

Dissociation Constants of Acetic acid in Aqueous Solution at 25°C

$\Lambda_0 = 390{\cdot}7$ ohm^{-1} cm^2 equiv^{-1}

Concentration $c \times 10^3$	Λ	$\alpha = \frac{\Lambda}{\Lambda_0}$	$K = \frac{C\alpha^2}{(1-\alpha)}$	K_{therm}
0·028014	210·38	0·53926	$1{\cdot}768 \times 10^{-5}$	$1{\cdot}752 \times 10^{-5}$
0·11135	127·75	0·327710	$1{\cdot}778 \times 10^{-5}$	$1{\cdot}753 \times 10^{-5}$
0·15321	112·05	0·28751	$1{\cdot}777 \times 10^{-5}$	$1{\cdot}750 \times 10^{-5}$
0·21844	96·493	0·24767	$1{\cdot}781 \times 10^{-5}$	$1{\cdot}750 \times 10^{-5}$
1·02831	48·146	0·12377	$1{\cdot}797 \times 10^{-5}$	$1{\cdot}750 \times 10^{-5}$
2·4140	32·217	0·08290	$1{\cdot}809 \times 10^{-5}$	$1{\cdot}750 \times 10^{-5}$
5·91153	20·962	0·054011	$1{\cdot}823 \times 10^{-5}$	$1{\cdot}748 \times 10^{-5}$

Example 1. *M/20 solution of acetic acid was found to be 1·89% dissociated. Calculate the dissociation constant of the acid*

Solution. We know that

$$K = \frac{c\,\alpha^2}{(1-\alpha)}$$

Here $c = \frac{1}{20} = 0{\cdot}05$ moles lit^{-1}

$$\alpha = 1{\cdot}89/100 = 0{\cdot}0189$$

$$\therefore \quad K = \frac{0{\cdot}05 \times (0{\cdot}0189)^2}{1 - 0{\cdot}0189} = 1{\cdot}821 \times 10^{-5}$$

Example 2. *The equivalent conductance of 0·02 M solution of acetic acid was found to be 11·57 ohm^{-1} cm^2 equiv^{-1} at 25°C. The equivalent ionic conductances of H^+ and CH_3COO^- ions at infinite dilution are 349·82 and 40·9 ohm^{-1} cm^2 equiv^{-1} respectively at the same temperature. Calculate the dissociation constant of acetic acid.*

Solution. We know that

$$K = \frac{c\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)}$$

Here $c = 0{\cdot}02$ moles lit^{-1}

$$\Lambda = 11{\cdot}57 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- = 40{\cdot}9 + 349{\cdot}82$$

$$= 390{\cdot}72 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$K = \frac{0{\cdot}02 \times (11{\cdot}57)^2}{390{\cdot}72(390{\cdot}72 - 11{\cdot}57)}$$

$$= 1{\cdot}807 \times 10^{-5}$$

Example 3. *If the degree of dissociation of N/10 acetic acid solution is 0·0133 at 25°C, what will be the degree of dissociation of N/50 acetic acid solution at the same temperature.*

Solution. (*i*) *Calculation of K*

We know that using approximate formula

$$K = c\alpha^2$$

Here $c = 1/10 = 0{\cdot}1$ mole lit^{-1}

$\alpha = 0{\cdot}0133$

$\therefore \quad K = 0{\cdot}1 \times (0{\cdot}0133)^2$

(*ii*) *Calculation of α for N/50 acetic acid solution*

We know that

$$K = c\alpha^2$$

Here $c = \dfrac{1}{50} = 0{\cdot}02$ mole lit^{-1}

$\therefore \; 0.1 \times (0{\cdot}0133)^2 = 0{\cdot}02 \times \alpha^2$

or $\alpha^2 = \dfrac{0{\cdot}1 \times (0{\cdot}0133)^2}{0{\cdot}02}$

or $\alpha = 0.02975$

Validity of Ostwald's Dilution Law. We have seen that Ostwald's dilution law is valid in case of weak electrolytes. When the law is applied to strong electrolytes like HCl, KCl, NaCl, etc., it fails completely. The value of dissociation constant does not come out to be constant at various concentrations. Table 6·2 shows the values of K for hydrochloric acid solution at 25°C at various concentrations. The value of K is not constant and goes on increasing with increasing concentration.

Table 6·2

Degrees of Dissociation and Dissociation Constant of Hydrochloric Acid calculated according to Ostwald Dilution law at 25°C.

$$\Lambda_0 = 426{\cdot}16 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

Concentration (moles lit^{-1})	*ohm^{-1} Λ cm^{2}equiv*	$\alpha = \Lambda/\Lambda_0$	$K = \dfrac{c\alpha^2}{1-\alpha}$
0·001	421·36	0·988	0·087
0.005	415·80	0·975	0.196
0·01	412·00	0·966	0·281
0·05	399.09	0·937	0·690
0·10	391·32	0·918	1·055
0·5	359·2	0·842	2·26
1·0	332·8	0·780	2·78

Limitations of Arrhenius Theory.

In the beginning of twentieth century it was realized that Arrhenius theory of electrolyte dissociation suffers from certain limitations and defects in the light of modern developments. Some important limitations are given below :

(*i*) Ostwald dilution law, which is based on Arrhenius theory does not give the constant value of K in case of stro

It means that the dissociation equilibrium, as postulated by Arrhenius, does not exist in strong electrolytes.

(*ii*) The degree of dissociation α calculated by Arrhenius from conductance ratio Λ/Λ_0 in case of strong electrolytes was not in agreement with that obtained from van't Hoff factor *i*.

(*iii*) According to ionic theory, the degree of dissociation of strong acids like HCl, H_2SO_4, HNO_3 etc.. should be different at a given concentration. Hence the heats of neutralization ΔH of these acids with a strong base should be different. Already, ΔH values of these acids with a strong base are too concordant to reflect the differences in the value of α.

(*iv*) The X-ray examination of NaCl crystal has revealed that it consists wholly of ions even in the solid state. Hence it cannot be understood how the dissolution of an ionic salt in water can form 'molecules' in the Arrhenius sense of the word.

(*v*) This theory does not explain the cause of ionization.

(*vi*) It does not incorporate interionic effects.

(*vii*) Strong electrolytes like NaCl, KCl, etc., conduct electricity even in the molten state. It shows that dissociation should have taken place in absence of water.

(*viii*) It was found experimentally that transport numbers vary with concentration. Dissociation theory could not explain these variations in transport numbers.

(*ix*) Absorption spectra of dilute solutions of strong electrolytes gave no evidence for the existence of undissociated molecules in dilute solutions.

Debye-Huckel Theory of Strong Electrolytes

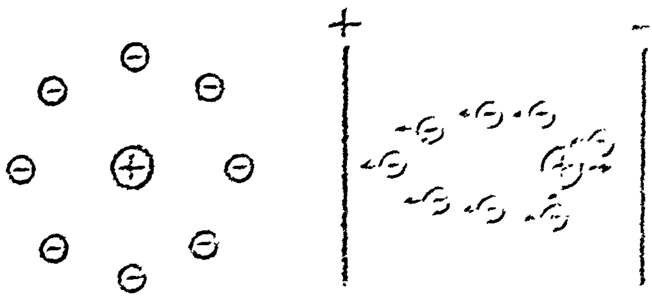
In the light of limitations discussed above it was felt that Arrhenius theory, though valid for weak electrolytes completely fails when applied to strong electrolytes Hence attempts were made by Sutherland, Bjerrum, Milner, and Ghosh to evolve a theory which could satisfactorily explain the behaviour of strong electrolytes, but they could achieve little success. In 1923 Debye and Huckel put forward the pioneering theory of strong electrolytes quantitatively which opened a new era in the study of electrochemistry. The theory was subsequently improved by Onsager (1926).

The fundamental postulate of this theory is that the strong electrolytes are completely dissociated at all reasonable concentrations. This idea is in accordance with the X-ray analysis of the crystal structures of electrovalent compounds, such as NaCl, KCl, etc., according to which these compounds consist of only ions even in the solid state. No molecules have been found to exist. When these electrovalent compounds are dissolved in water, it is reasonable to assume that the ion, which already existed in solid state, become free to move in solution and are able to conduct electricity. Thus,

strong electrolytes are completely *ionized* as well as *dissociated* in solution at all reasonable concentrations. If such is the case, then the change in equivalent conductance cannot be attributed to the change in the degree of dissociation, because degree of dissociation is always unity. Hence the variation of conductance with concentration must be due to the change in ionic speeds. When the solution of electrolyte is infinitely dilute, then the ions are far apart and they exert negligible influence on one another. When the concentration of the solution is increased, then the ions come closer and **interionic attraction** develops, which results in the decrease of ionic speeds. Hence the equivalent conductance decreases. Thus, *the fall in equivalent conductance with increasing concentration is due to the decrease in ionic speeds on account of interionic attraction, and not partial dissociation.* This is the basis of Debye Huckel theory in its simplest ~~from.~~ form.

When a electric potential is applied to the solution of a strong electrolyte, the ions do not move towards electrodes in straight lines. Their motion is through a zig-zag path similar to Brownian movement, but the average drift of the ion is towards electrodes in an electric field. According to Debye-Huckel theory, the ionic speeds, in the presence of applied potential, are retarded by the two effects as given below :

1. Asymmetry or Relaxation Effect. *It was postulated by the theory that due to the attraction between the oppositely charged ions* ~~theory that due to the attraction between~~ *the oppositely charged atmosphere of oppositely charged ions in the absence of any applied potential. Such an atmosphere of oppositely charged ions is called an*



On applying a potential the cation moves towards cathode. The ionic atmosphere has some inertia, hence it cannot adjust itself to the new position of the moving ion instantaneously. In other words, ionic atmosphere requires some *relaxation time* to readjust itself with the moving ion. As a result of this, the ionic atmosphere becomes asymmetric as shown in Fig. 6·1 (*ii*) and there is a net accumulation of opposite charge behind the moving ion. This accumulated opposite change exerts an electrostatic drag in the direction opposite to the motion of the ion causing its speed to decrease. This effect on the speed of the ion is known as **asymmetric** or **relaxation effect,** because it arises due to the asymmetry or relaxation of the ionic atmosphere.

2. Electrophoretic Effect. It arises due to the fact that the ionic atmosphere itself moves in a direction opposite to that of the central ion. Moreover, the ions of the atmosphere are also solvated so that they tend to carry the solvent molecules associated with them. Thus, there results a net flow of solvent molecules in a direction opposite to that of the motion of central ion which itself is also solvated. Consequently, the central ion has to make its way against the counter flow of solvent molecules in opposite direction. Hence the speed of the ion decreases. This effect on the speed of the ion is known as **electrophoretic effect,** because it is analogous to the electrophoresis in colloids.

Debye and Huckel obtained the steady state of motion of the ion by equating the electric driving force to the sum of retardations caused by asymmetric and electrophoretic effects. They calculated the magnitude of each of the effect and derived the equation for the equivalent conductance of an electrolyte, which was subsequently improved by Onsagar. Hence the equation is known as **Debye-Huckel-Onsager equation** or in short **Onsager equation** as given below.

$$\Lambda = \Lambda_0 - \left[\frac{82{\cdot}48}{(\epsilon T)^{\frac{1}{2}}\eta} + \frac{8{\cdot}20 \times 10^5}{(\epsilon T)^{\frac{3}{2}}} \Lambda_0 \right] c^{\frac{1}{2}} \qquad ...(6{\cdot}10)$$

where Λ_0 is the equivalent conductance of the electrolyte at infinite dilution, ϵ and η are the dielectric constant and viscosity of the medium respectively, T is the absolute temperature, and c is the concentration of the electrolyte in moles lit^{-1}

As Λ_0 for an electrolyte is constant and so also is ϵ for a given solvent, it can be seen from Eq. (6·10) that Λ decreases with increase of concentration in a given solvent and at a constant temperature. This fall in equivalent conductance is partially due to electrophoretic effect and partially due to asymmmetric effect. In the bracket, the first term is due to the electrophoretic effect and the second term is due to asymmetric effect. The sum of these two terms multiplied with the square root of concentration gives the difference between Λ_0 and Λ.

Verification of Debye-Huckel-Onsager Equation

If the equivalent conductance of a solution of electrolyte is measured at various concentrations in the same solvent at a particular temperature, then Eq. (6·10) can be written as

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c} \qquad \ldots(6{\cdot}11)$$

where A and B are constants. Since Λ_0 is constant for an electrolyte, Eq. (6·11) is a linear relation between Λ and $\sqrt{c}$. Thus, if Λ is plotted against $\sqrt{c}$, a straight line should be obtained according to Onsager equation. The experimental values of Λ and $\sqrt{c}$ have been plotted for various electrolytes and actually straight lines have been obtained at low concentrations as shown in Fig. 6·2. Moreover, the slopes of the straight lines obtained from the graphitally with those calculated from Eq. (6·10). Thus, the Onsager equation is verified experimentally at low concentrations. At infinite dilution c approaches zero so that the second term in the Eq. (6·11) becomes negligible and Λ approaches Λ_0 in accordance with the experiment.

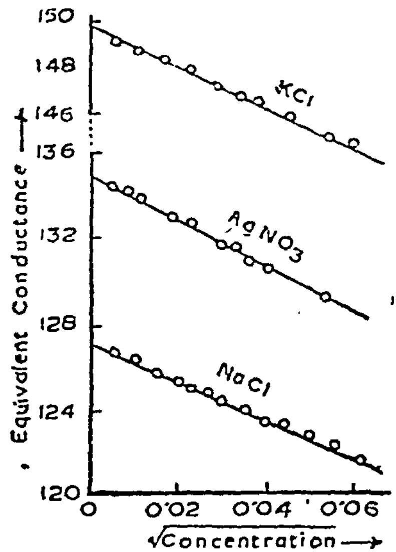


Fig. 6·2. Plot between Λ and $\sqrt{c}$ for Various Electrolytes.

Further confirmation for the correctness of Debye-Huckel theory have been obtained from a number of effects occurring in couductance experiments. It can be seen in Eq. (6·10) that the dielectric constant ϵ appears in the denominator of both the terms in bracket. This means that the equivalent conductance must fall with increase in concentration more rapidly in the solvent of low dielectric constant than in water. Experiments with solvents like ethyl alcohol, acetonitrile, etc., having low values of dielectric constant have actually supported this conclusion.

As the frequency of alternating current is increased, a point is reached when ionic atmosphere cannot follow the rapidly varying

field. As a result of this, ions move independent of each other and the increase in conductance is expected. This has actually been observed with A.C. frequency of the order of 3×10^6 cycles sec^{-1} and the effect is known as **Debye—Falkenhagen effect.**

Another support for the theory is obtained by the study of conductance of electrolytes at high field strengths, *i.e.*, of the order of 10^5 volts cm^{-1}. At such high field strengths it is expect thated the ionic speeds become so large that ionic atmosphere should be left behind and the ions should move freely. This should result in the increase of conductance, which has actually been observed. This effect is known as **Wien effect.**

It must, however, be noted that Onsager equation gives excellent agreement with experimental conductance data at low concentration. The range of validity becomes higher in the case of uni-univalent electrolytes.

Activity and Activity Coefficient.

Consider the dissociation equilibrium of acetic acid,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

the dissociation constant K of which is given by

$$K = \frac{c_{H^+} \times c_{CH_3COO^-}}{c_{CH_3COOH}} \qquad ...(6{\cdot}12)$$

K can be given in terms of degree of dissociation α of acetic acid its concentration in moles lit^{-1} as

$$K = \frac{\alpha^2 c}{(1-\alpha)} \qquad ...(6{\cdot}13)$$

The values of K found from Eq. (6·13) have been shown in Table 6·1. A closer examination of the values of K in the table shown that they are not strictly constant. The value of K goes on increasing gradually with increasing concentration. What is the cause of this drift in the value of K ? It can be explained in the following manner.

The quantities used in the law of mass action are active masses, which have been stated to be proportional to molar concentrations. In solutions of electrolytes the freedom of molecules and ions are affected by interionic and ion-dipole interactions. Ions of opposite charge are attracted towards each other and those of similar charge are repelled. In addition to this, solvated ions are also formed due to ion-dipole attraction. The net effect of all these interactions is that a solution of electrolyte, like CH_3COOH behaves as if its concentration were greater, equal to, or less than the actual concentration. Thus, the effective concentration of acetic acid in solutions may differ from its actual concentration depending upon the relative magnitudes of interionic and ion-dipole interactions. It is, therefore, clear that

the electrolytic solutions may behave in such a way that their actual concentration is not effective. As we used the actual concentrations in the calculation of K from Eq. (6·13), it does not come out to be strictly constant. Similar deviations are observed in the study of colligative properties of electrolytes, if we use actual concentration terms. These deviations are enhanced particularly in case of strong electrolytes, because strong electrolytes are almost completely ionised, which results in the increase of inter-ionic and ion-dipole interactions.

It was suggested that if effective concentrations are substituted for active masses, then the mathematical forms of various laws involving concentration terms are also maintained and the expressions of the laws can be applied to real systems. Lewis suggested the term **activity** for *effective concentraction.* It is represented by a. Thus, if activities of various chemical species are substituted for concentration terms in Eq. (6·12), then it takes the form,

$$K = \frac{a_{H^+} \times a_{CH_3COO^-}}{a_{CH_3COOH}} \qquad ...(6·14)$$

where K is the true (thermodynamic) constant. Its value is constant and is independent of the concentration of acetic acid as can be seen in the last column of Table 6·1. The activity of a chemical species is related to the molar concentration c and is defined by the following expression,

$$a = f\,c \qquad ...(6·15)$$

where f is a factor, called **activity coefficient.** Rearranging Eq. (6·15) we get

$$f = \frac{a}{c} \qquad ...(6·16)$$

Thus, **activity coefficient** may be defined as *the ratio of activity to actual concentration.*

According to conventions, if concentration is expressed in molality m *i.e.*, moles per 1000 gm of solvent, then the activity coefficient is denoted by γ. Thus, Eq. (6·16) takes the form

$$\gamma = \frac{a}{m} \qquad ...(6·17)$$

In aqueous solutions, molarity and molality are almost equal and therefore the value of f and γ are almost same. In more concentrated solutions f and γ will have different values.

At infinite dilutions, the ions are drawn far apart and the interionic interaction becomes negligible. In such situations, the value of activity coefficient approaches unity and according to Eq. (6·[illegible]),

we may say that activity and actual concentration become identical. In other words, we mean that the real systems approach the ideal behaviour. At appreciable concentrations, interionic forces develop and the values of f depart from unity. In other words, we say that the real systems depart from ideal behaviour. Thus, activity coefficient expresses the departure from ideal behaviour. Various laws involving concentration terms are applicable to ideal systems only, but these laws in terms of activities are quite general and can be applied to ideal as well as real systems. In case of strong electrolytes, there is a remarkable departure from ideal behaviour except at infinite dilution. Hence the activity coefficients differ markedly from unity and also change with concentration.

Mean Activity of an Electrolyte. It must be noted that the activities or activity coefficient of a particular type of ion cannot be determined experimentally because it is impossible to prepare a solution containing only one type of ion, However, it is convenient to relate the activity of an electrolyte, which is a measurable quantity to the individual activities of the ions into which it dissociates. For example, KCl dissociates in solution according to equation

$$KCl \rightleftharpoons K^+ + Cl^-$$

The activity of KCl can be determined experimentally. If a denotes the activity of KCl and a_+ and a_- denote the activities of cations and anions respectively, then we can write as *definitions*

$$a = a_+ a_- = a^2_\pm \qquad \text{...(6·18)}$$

or $$a_\pm = \sqrt{a_+ a_-} = \sqrt{a} \qquad \text{...(6·19)}$$

Thus, we see that the quantity $a_\pm$ is the geometric mean of a_+ and a_-, hence it is called **mean activity** of the ions. In the same way if f_+ and f_- are the activity coefficients of cations and anions respectively then the **mean activity coefficient** $f_\pm$ of the ions will be given by the expression

$$f_\pm = \sqrt{f_+ f_-} \qquad \text{...(6·20)}$$

Now consider a general electrolyte A_xB which dissociates into x ions of A, each having charge z_+ and y ions of B, each having charge z_-, according to the equation

$$A_x B_y \rightleftharpoons xA^{z+} + yB^{z-}$$

The activity a of the electrolyte is given by

$$a = a^x_+ a^y_- = a_\pm{}^{x+y} \qquad \text{...(6·21)}$$

$$\text{or } a_\pm = [a_+^x\, a_-^y]^{1/(x+y)} = a^{1/(x+y)} \qquad \text{...(6·22)}$$

Similarly, the mean activity coefficient $f_{\pm}$, is given by

$$f_{\pm} = [f_+^{x} f_-^{y}]^{1/(x+y)} \quad ...(6{\cdot}23)$$

The relation between mean activity and mean activity coefficient can be obtained in the following way.

The individual ionic activity coefficients are given by

$$a_+ = f_+ c_+ \text{ and } a_- = f_- c_-$$

where c_+ and c_- are the concentrations of cations and anions respectively. Substituting these values of a_+ and in Eq. (6·21), a_- we get

$$a = c_+^{x}\, c_-^{y}\, f_+^{x}\, f_-^{y}$$

Substituting the value of a in Eq. (6·22)

$$a_{\pm} = a^{1/x+y} = [c_+^{x}\, c_-^{y}\, f_+^{x}\, f_-^{y}]^{1/x+y} \quad ...(6{\cdot}24)$$

Substituting Eq. (6 23) in Eq. (6·25), we get

$$a_+ = [c_+^{x}\, c_-^{y}]^{1/x+y}\, f_{\pm}$$

$$\text{or } f_{\pm} = \frac{a_{\pm}}{[c_+^{x}\, c_-^{y}]^{1/(x+y)}} \quad ...(6{\cdot}25)$$

If the concentration of the solution is c, then

$$c_+ = x\,c \text{ and } c_- = y\,c$$

Substituting in Eq. (6·25), we obtain

$$f_{\pm} = \frac{a_{\pm}}{c(x^{x}y^{y})^{1/x+y}} = \frac{a_{\pm}}{c_{\pm}} \quad ...(6{\cdot}26)$$

where $c_{\pm} = c\,(x^{x}y^{y})^{1/x+y}$ ...(6·27)

$c_{2\pm}$ is called the **mean molarity** of the solution.

To illustrate the various relations obtained above, let us take an example of $Al_2(SO_4)_3$ which dissociates in solution according to the equation

$$Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$$

In this case, $x = 2$, and $y = 3$

According to Eq. (6·21),

$$a = a_+^{2}\, a_-^{3} = a_{\pm}^{5}$$

$$\text{or } a_{\pm} = a^{1/5}$$

According to Eq. (6·23)

$$f_{\pm} = [f_+^{2}\, f_-^{3}]^{1/2+3} = [f_+^{2} f_-^{3}]^{1/5}$$

Again, from Eq. (6·26)

$$f_{\pm} = \frac{a_{\pm}}{c(2^{2}\,3^{3})^{1/2+3}} = \frac{a_{\pm}}{(108)^{1/5}\,c}$$

Now it is clear that if we know the activity of an electrolyte at a particular concentration in the solution, the mean activity can be obtained from Eq. (6·21) and the mean activity coefficient can be obtained from Eq. (6·26)

If the concentration is expressed in terms of **molality**, Eqs. (6·23), (6·26) and (6·27) will have the following forms :

$$\gamma_{\pm} = [\gamma_{+}^{x}\,\gamma_{-}^{y}]^{1/x+y} \qquad \ldots(6{\cdot}28)$$

$$\gamma_{\pm} = \frac{a_{\pm}}{m\,(x^{x}\,y^{y})^{1/x+y}} = \frac{a_{\pm}}{m_{\pm}} \qquad \ldots(6{\cdot}29)$$

and $$m_{\pm} = m\,(x^{x}\,y^{y})^{1/x+y} \qquad \ldots(6{\cdot}30)$$

where $m_{\pm}$ is called the **mean molality** of the solution.

A number of methods for determining activities are known. These methods are based on measurements of freezing point depression, boiling point elevation, emf, etc.

Example 4. *The mean activity coefficient of 0·1 m $ZnCl_2$ solution is 0·502. Calculate (i) the mean molality, (ii) the mean ionic activity, and (iii) the activity of the salt.*

Solution. $Zn\,Cl_2$ dissociates in solution as

$$ZnCl_2 = Zn^{2+} + 2Cl^-$$

(*i*) We know that

$$m_{\pm} = m\,(x^{x}y^{x})^{1/x+y}$$

Here $m = 0{\cdot}1,\ x = 1,\ y = 2$

$\therefore$ $m_{\pm} = 0{\cdot}1\,(1^1\times2^2)^{1/1+2} = 0{\cdot}1\times(4)^{1/3}$

$= 0{\cdot}1588$

(*ii*) We know that

$$a_{\pm} = m_{\pm}\,\gamma_{\pm}$$

Here $m_{\pm} = 0{\cdot}1588$

$\gamma_{\pm} = 0{\cdot}502$

$\therefore$ $a_{\pm} = 0{\cdot}1588\times0{\cdot}502$

$= 0{\cdot}07969$

(*iii*) We know that

$$a = (a_{\pm})^{x+y}$$

Here $a_{\pm} = 0{\cdot}07958$

$x = 1$ and $y = 2$

$\therefore$ $a = (0{\cdot}07958)^{1+2} = (0{\cdot}07958)^3$

$= 0{\cdot}0005060$

Example 5. *The mean activity coefficient of 0·01M $CdCl_2$ is 0·524. Calculate the mean ionic activity.*

Solution. $CdCl_2$ dissociates in solution as

$$CdCl_2 = cd^{2+} + 2Cl^-$$

We keow that

$$a_{\pm} = c\,(x^{x}y^{y})^{1/x+y}\,f_{+}$$

Here $c = 0{\cdot}01,\ x = 1,\ y = 2,$ and $f_\pm = 0{\cdot}524$

$$\therefore \quad a_\pm = 0{\cdot}01\ (1^1 \times 2^2)^{1/1+2} \times 0{\cdot}524$$
$$= 0{\cdot}01 \times (4)^{1/3} \times 0{\cdot}524$$
$$= 0{\cdot}0130$$

Variation of Mean Activity Coefficients with Concentration.

The mean activity coefficients of a number of electrolytes have been determined at various concentrations. The results are shown in Table 6·3.

Table 6·3

Mean Activity Coefficients of Electrolytes in Water at 25°C

Molality	*HCl*	*NaCl*	*$CdCl_2$*	*$ZnCl_2$*	*$ZnSO_4$*	*$CdSO_4$*	*H_2SO_4*
0·001	0·965	0·965	0·819	0·881	0·700	0·697	0·830
0·005	0·929	0·927	0·623	0 767	0·477	0·476	0·639
0·01	0·905	0·902	0·524	0 708	0·387	0·383	0·544
0·05	0·830	0·819	0·304	0·556	0·202	0·199	0·340
0·10	0·793	0·778	0·228	0·502	0·148	0·150	0·265
0·50	0·757	0·681	0·100	0·376	0·063	0·061	0·154
1·00	0·809	0·657	0·066	0·325	0·043	0·041	0·130
2·00	1·009	0 668	0·044	—	0·035	0·032	0·124
4·00	1·762	0·783	—	—	—		0·171

If the variation of mean activity coefficients with concentration is closely examined from Table 6·3, then the following facts are revealed :

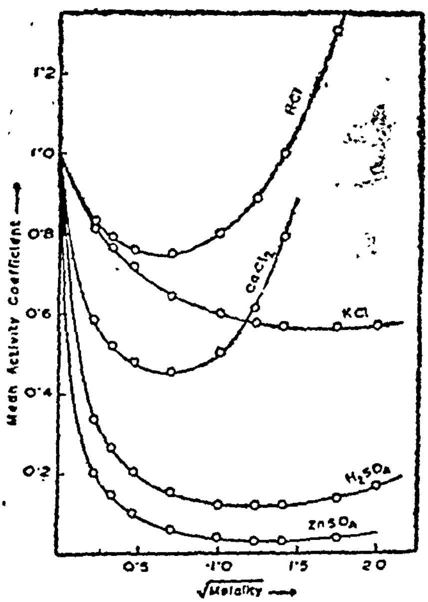


Fig. 6·3. Plot of Mean Activity Coefficients *vs.* Square root of Molality.

(*i*) As the concentration of the electrolyte is increased, the value of mean activity coefficient first falls, passes through a minimum and then increases again. This is also illustrated in Fig. 6·3, in which the mean activity coefficient is plotted against square root of molality for various electrolytes. It is also seen from the figure that the value of mean activity coefficient of all electrolytes approach unity at infinite dilution.

(*ii*) In very dilute solutions same type of electrolytes, *e.g.*, uni-univalent electrolytes like HCl and NaCl, have almost same values of mean activity coefficients at the same concentration.

(*iii*) At a given concentration, higher the product of valence of two ions, greater will be the departure of activity coefficient from unity.

Ionic Strength

In order to express the change in mean activity coefficient with concentration quantitatively, Lewis and Randall introduced the concept of **ionic strength.** As we have already seen that many properties of electrolytic solutions depend upon the electrostatic interactions between the ions. As for example, the electrostatic force between a pair of doubly charged ions is four times than that between a pair of singly charged ions, Ionic strength is such a function of ionic concentration which involves all such effects of ionic charges. As the electrostatic interactions between ions in a solution are primarily responsible for the deviation of an ionic solute from ideal behaviour, ionic strength is a good measure of the nonideality that the solution imposes on a given dissociated electrolyte in solution. **Ionic strength,** represented by μ, is characteristic of the solution and is defined as *half the sum of all terms obtained as the product of concentration and the square of valence for each ionic species present in the solution.* Thus, if c_1, c_2, c_3, etc., are the concentrations in molality or molarity of different ionic species indicated by subscripts 1, 2, 3, etc., and Z_1, Z_2, Z_3, etc., are their corresponding charges, then

$$\mu = \tfrac{1}{2}(c_1Z_1^2 + c_2Z_2^2 + c_3Z_3^2 + \ldots + c_iZ_i^2)$$

or

$$\mu = \tfrac{1}{2}\sum_i c_iZ_i^2 \qquad \ldots(6{\cdot}27)$$

where c_i is the concentration of *i*th ion and Z_i is its charge. The summation is carried over all the ions present in the solution. Ionic strength is also defined by Eq. (6·27).

It was pointed out by Lewis and Randall that *the mean activity coefficient of any given electrolyte in very dilute solution is the same in all solutions of the same ionic strength.* It is known as **Lewis-Randall rule.** Thus, if the ionic concentration of a solution is kept constant by the addition of neutral salts, the mean activity coefficient of a given electrolyte should remain the same.

The ionic strength of an aqueous solution of a uni-univalent electrolyte like HCl, NaCl, etc., is given by

$$\mu = \tfrac{1}{2}\,(c_1 Z_1^2 + c_2 Z_2^2)$$

the two terms in the bracket correspond to positive and negative ions of the electrolyte. In this case, $Z_1 = Z_2 = 1$ and $c_1 = c_2$, hence

$$\mu = c$$

where c is the concentration of the electrolyte. Thus, the ionic strength is equal to the concentration in the case of a uni-univalent electrolyte. For other electrolytes, ionic strength and the concentration of the electrolyte differ considerably. This can be seen from the following example.

Example 6. *Calculate the ionic strength of the solution containing (i) 0·1 M HCl (ii) 0·2 M H_2SO_4 (iii) 0·01 M $Cr_2(SO_4)_3$ (iv) 0·02 M Nacl and 0·02 M Na_2SO_4.*

Solution.

(*i*) For 0·1 *M* HCl solution, which dissociates as

$$HCl \rightarrow H^+ + Cl^-$$

We know that

$$\mu = \tfrac{1}{2}(c_1 Z_1^2 + c_2 Z_2^2)$$

Here $c_1 = 0{\cdot}1,\quad c_2 = 0{\cdot}1,\quad Z_1 = 1,$ and $Z_2 = 1$

$$\therefore \quad \mu = \tfrac{1}{2}(0{\cdot}1 \times 1^2 + 0{\cdot}1 \times 1^2 = 0{\cdot}1$$
$$= 0{\cdot}1$$

(*ii*) For 0·2 *M* H_2SO_4 solution, which dissociates as

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

We know that

$$\mu = \tfrac{1}{2}(c_1 Z_1^2 + c_2 Z_2^2)$$

Here $c_1 = 2 \times 0{\cdot}2 = 0{\cdot}4,\quad c_2 = 0{\cdot}2,\quad Z_1 = 1,$ and $Z_2 = 2$

$$\therefore \quad \mu = \tfrac{1}{2}(0{\cdot}4 \times 1^2 + 0{\cdot}2 \times 2^2) = 0{\cdot}6$$

(*iii*) For 0·01 *M* $Cr_2(SO_4)_3$ solution which dissociates as

$$Cr_2(SO_4)_3 \rightarrow 2Cr^{3+} + 3SO_4^{2-}$$

We know that

$$\mu = \tfrac{1}{2}(c_1 Z_1^2 + c_2 Z_2^2)$$

Here $c_1 = 2 \times 0{\cdot}01 = 0{\cdot}02,\quad c_2 = 3 \times 0{\cdot}01 = 0{\cdot}03$

$Z_1 = 3,$ and $Z_2 = 2$

$$\therefore \quad \mu = \tfrac{1}{2}(0{\cdot}02 \times 3^2 + 0{\cdot}03 \times 2^2)$$
$$= 0{\cdot}15.$$

(*iv*) For a solution containing 0·02 *M* NaCl and 0·02 *M* Na_2SO_4, there are three types of ions. *viz.* Na^+, Cl^- and SO_4^{2-} ions in the solution. We know that,

$$\mu = \tfrac{1}{2}(c_1 Z_1^2 + c_2 Z_2^2 + c_3 Z_3^2)$$

Here, for Na^+ ion, $c_1 = 0{\cdot}02 + 2 \times 0{\cdot}02$
$= 0{\cdot}06$

$Z_1 = 1$

For Cl^- ion. $c_2 = 0{\cdot}02 \quad Z_2 = 1$

For SO_4^{2-} ion $c_3 = 0{\cdot}02, \quad Z_3 = 2$

$$\mu = \tfrac{1}{2}(0{\cdot}06 \times 1^2 + 0{\cdot}02 \times 1^2 + 0{\cdot}02 \times 2^2)$$
$$= 0{\cdot}08$$

Dependence of Mean Activity Coefficient on Ionic Strength : The Debye-Huckel Limiting Law.

Debye-Huckel theory gave an expression for the mean activity coefficient $f_{\pm}$ of an electrolyte in aqueous solution at 25°C in terms of ionic strength μ as given below :

$$\log f_{\pm} = -0.509\ Z_{+}Z_{-}\sqrt{\mu} \qquad ...(6.28)$$

where Z_{+} and Z_{-} are the numbers of electric charges of cation and anion of the electrolyte respectively, without regard to the sign. Eq. (6.28) represents the **Debye-Huckel limiting law** and expresses the dependence of $f_{\pm}$ on μ. The word 'limiting' is used because the derivation of the equation is such that it can be used for very dilute solutions approaching the limit of infinite dilution. The Debye-Huckel limiting law is in good agree- ment with the experimental conclusion for the variation of $f_{\pm}$ with c, shown in Table 6.3, as discussed below :

(*i*) Eq. (6.28) shows that $\log f_{\pm}$ is negative and hence $f_{\pm}$ is less than one in very dilute solutions according to Table 6.3.

(*ii*) For a given electrolyte Z_{+} and Z_{-} are constants. Hence it can be seen from Eq (6.28) that the mean activity coefficient will be the same for all solution of the same ionic strength. This is in accordance with Lewis and Randall's empirical rule.

(*iii*) For all electrolytes of the same valence type *e g.*, uni-univalent electrolytes like HCl, KCl and NaCl, Z_{+} and Z_{-} are the same. Hence $f_{\pm}$ should be the same at equal ionic strengths or concentrations, which is in accordance with experimental data at large dilutions.

(*iv*) From Eq. (6.28) it is seen that $\log f_{\pm}$ which is a measure of departure of $f_{\pm}$ from unity, should be proportional to the product $Z_{+}Z_{-}$. Thus higher the product $Z_{+}Z_{-}$, greater is the departure of $f_{\pm}$ from unity. It is also in accordance with the experimental data shown in Table 6.3.

(*v*) The form of Eq. (6.28) shows that $-\log f_{\pm}$ is plotted against $\sqrt{\mu}$, then a straight line should be obtained. Experimentally, it has actually been verified.

Thus, the Debye Huckel limiting law should be considered to have a strong experimental basis. It should, however, be noted that the law is applicable to those dilute solutions only whose ionic strengths are less than 0.01. The success of Debye-Huckel theoretical law for such very dilute solutions is really a great triumph. Hence an electrolytic solution should not be considered simply in terms of individual ions. The interionic interactions should be taken into

view, because they determine the properties of these ionic solutions in the same way as the intermoleculer interactions in gases determine the properties of real gases.

Example 7. *Calculate the mean activity coefficient of (i) KCl in 0·0009 M aqueous solution and (ii) $BaCl_2$ in 0·005 M aqueous solution, at 25°C.*

Solution. (i) For KCl, in 0·0009 *M* solution, which dissociates as

$$KCl \rightarrow K^+ + Cl^-$$

We know that

$$\log f_\pm = \cdot 0509\, Z_+ Z_- \sqrt{\mu}$$

Here $Z_+ = 1.\ Z_- = -1, \mu = c = 0\cdot0009$

$\therefore$ $\log f_\pm = 0\cdot509\,(1)\,(-1)\sqrt{0\cdot0009}$

or $\log f_\pm = -0\cdot01527$

$\therefore$ $f_\pm = 0\cdot9655$

(ii) For $BaCl_2$, in 0·005 *M* solution, which dissociates as

$$BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$$

We know that, $\mu = \frac{1}{2}(c_1 Z_1^2 + c_2 Z_2^2)$

Here $c_1 = 0\cdot005.\ Z_1 = 2,\ c_2 = 2\times0\cdot005 = 0\cdot01,\ Z_2 = 1$

$\therefore$ $\mu = \frac{1}{2}(0\cdot005\times2^2 + 0\cdot01\times1^2) = 0\cdot015$

Again, we know that

$$\log f_\pm = 0\cdot509\, Z_+ Z_- \sqrt{\mu}$$

Here $Z_+ = 2,\ Z_- = -1,\ \mu = 0\cdot015$

$\therefore$ $\log f_\pm = 0\cdot509(2)(-1)\sqrt{0\cdot015}$

$= -0\cdot1247$

$\therefore$ $f_\pm = 0\cdot7504$

TEST YOUR KNOWLEDGE

1. Complete the following :

(i) $K = \dfrac{\ldots\alpha^2}{1-\alpha}$

(ii) $K = \dfrac{c\Lambda^2}{\ldots(\Lambda_0 - \Lambda)}$

(iii) $\Lambda = \Lambda_0 - \left[\dfrac{82\cdot48}{(\ldots\ldots)^{\frac{1}{2}}\eta} + \dfrac{8\cdot20\times10^5}{(\epsilon T)^{3/2}}\right]$

(iv) $\ldots\ldots = fc$

(v) $\ldots\ldots = [f_+^x f_-^y]^{1/x+y}$

(vi) $f_\pm = \dfrac{a_\pm}{(x^x y^y)^{1/x+y}}$

(vii) $\mu = \frac{1}{2}\sum_i c_i^2\ldots\ldots$

(viii) $\log f_\pm = -0\cdot509\, Z_+ Z_- \ldots\ldots$

2. Give a term for each of the following :

(i) Retardation in the speed of an ion from the electrostatic drag caused

(*ii*) Atmosphere of oppositely charged ions around a particular ion.
(*iii*) Decrease in the speed of an ion by the counter flow of solvent molecules in opposite direction.
(*iv*) Increase in conductance at high a.c.f requency.
(*v*) Increase in conductance at high field strengths.
(*vi*) The ratio of activity to actual concentration.

3. Fill in the blanks with appropriate words :
(*i*) The degree of dissociation increases with...
(*ii*) The properties of an electrolytic solution are the properties of its...
(*iii*) Ostwald dilution law is valid for...electrolytes.
(*iv*) Debye-Huckel postulated that...electrolytes are completely dissociated at all reasonable concentrations.
(*v*) The fall in equivalent conductance with increasing concentration is due to ..in ionic speeds on account of......
(*vi*) Equivalent conductance...with increase in concentration more rapidly in the solvents of lower...than in water .
(*vii*) At infinite dilution the value of activity coefficient approaches....
(*viii*) For a given electrolyte, $f\pm$ is the same in all very dilute solutions of the same....
(*ix*) Higher the product Z_+Z_-,...is the departure of $f\pm$ from unity.
(*x*) In very dilute solutions, same type of electrolytes have almost identical values of...at the same concentration.

KEY

1. (*i*) c (*ii*) $\wedge_0$ (*iii*) ϵT, $c^{1/2}$ (*iv*) a (*v*) $f\pm$ (*vi*) c (*vii*) Zi^2 (*viii*) $\sqrt{\mu}$
2. (*i*) Relaxation or asymmetric effect (*ii*) Ionic atmosphere (*iii*) Electrophoretic effect.
(*iv*) Debye-Falkenhagen effect (*v*) Wien effect (*vi*) Activity coefficient.
3. (*i*) Dilution (*ii*) ions (*iii*) weak (*iv*) strong (*v*) decrease, interionic attraction (*vi*) falls, dielectric constant (*vii*) unity (*viii*) ionic strength (*ix*) greater (*x*) mean activity coefficient.

QUESTIONS

1. Give the main features of Arrhenius theory of electrolytic dissociation, What are the evidence in its favour ? Give its limitations.
2. Derive a general expression of Ostwald dilution law for the equilibrium

$$A_x\ B_y = xA^{z+} + yB^{z-}$$

and deduce the relation of dissociation constant for uni-univalent electrolyte from it in terms of equivalent conductances. How is the law verified ? Give its limitations.
3. Discuss the Debye-Huckel theory of strong electrolytes. How is it verified ?
4. Explain the terms 'activity' and 'activity coefficient'? What are the significances of these terms ? Derive the expression for the 'mean activity' and 'mean activity coefficients' for a general electrolyte $A_x\ B_y$.
5. How do the mean activity coefficients vary with concentration and show how these results are explained by Debye-Huckel limiting law ?
6. Define and explain the term 'ionic strength' of a solution. What does it signify ?
7. Write short notes on the following :
(i) Activity and activity coefficient.
(ii) Ionic strength.

(*ii*) Atmosphere of oppositely charged ions around a particular ion.
(*iii*) Decrease in the speed of an ion by the counter flow of solvent molecules in opposite direction.
(*iv*) Increase in conductance at high a.c.f requency.
(*v*) Increase in conductance at high field strengths.
(*vi*) The ratio of activity to actual concentration.

3. **Fill in the blanks with appropriate words :**
(*i*) The degree of dissociation increases with...
(*ii*) The properties of an electrolytic solution are the properties of its...
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(*v*) The fall in equivalent conductance with increasing concentration is due to ..in ionic speeds on account of......
(*vi*) Equivalent conductance...with increase in concentration more rapidly in the solvents of lower...than in water .
(*vii*) At infinite dilution the value of activity coefficient approaches....
(*viii*) For a given electrolyte, $f\pm$ is the same in all very dilute solutions of the same....
(*ix*) Higher the product Z_+Z_-,...is the departure of $f\pm$ from unity.
(*x*) In very dilute solutions, same type of electrolytes have almost identical values of...at the same concentration.

KEY

1. (*i*) c (*ii*) $\wedge_0$ (*iii*) ϵT, $c^{1/2}$ (*iv*) a (*v*) $f\pm$ (*vi*) c (*vii*) Zi^2 (*viii*) $\sqrt{\mu}$
2. (*i*) Relaxation or asymmetric effect (*ii*) Ionic atmosphere (*iii*) Electrophoretic effect.
(*iv*) Debye-Falkenhagen effect (*v*) Wien effect (*vi*) Activity coefficient.
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QUESTIONS

1. Give the main features of Arrhenius theory of electrolytic dissociation, What are the evidence in its favour ? Give its limitations.
2. Derive a general expression of Ostwald dilution law for the equilibrium
$$A_x\, B_y \rightleftharpoons xA^{z+} + yB^{z-}$$
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7. Write short notes on the following :
(i) Activity and activity coefficient.
(ii) Ionic strength.

7

Electromotive Force

Introduction

We have already studied the electrolysis in which the chemical reaction takes place when electric current is passed through the solution of an electrolyte. In this process the electric energy is converted into chemical energy. A reverse process, *i.e.* conversion of chemical energy into electrical energy is also possible. The devices used for these conversions are commonly known as **cells.** The cells used for converting electrical into chemical energy are called **electrolytic cells** and those used for conversion of chemical into electrical energy are called **galvanic cells** or in modern usage, **electro-chemical cells.** We have already studied much about electrolytic cells in chapter 5. In this chapter we shall deal with galvanic cells and their use for the production of electric current at the cost of physio-chemical changes occurring inside the cell.

Galvanic Cells

A galvanic cell is a device in which two electrodes, which must be metallic or ionic conductors, are immersed in one or more suitable electrolytes. Out of various types of galvanic cell we shall discuss a simple cell-the **Daniell cell** designed by J. F. Daniell in the beginning of nineteenth century. It is commonly used in laboratories. It consists of a zinc electrode immersed in a zinc sulphate solution and a copper electrode immersed in a copper sulphate solution. The two solutions are separated from each other by means of a porous pot as shown in Fig. 7·1. The porous pot prevents the direct mixing of the solutions. When the metallic electrodes are connected by a wire, the current flows through the circuit as indicated by the voltmeter V connected in the circuit which records a voltage of about 1·1 volt.

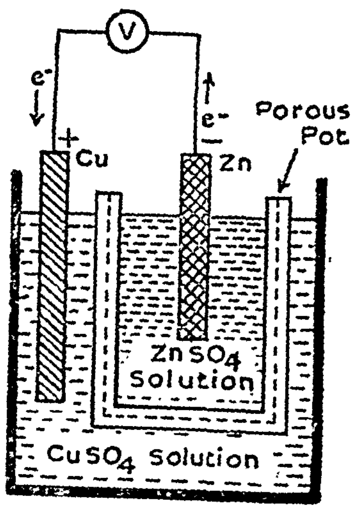

Fig. 7·1 The Daniell Cell

cell is applied, an *infinitesimal* current will flow and the reaction will take place according to Eq. (7·5.) Now if the opposing emf is increased so that it becomes infinitesimally greater than the emf of the cell, the current flows in the opposite direction. Now Cu dissolves with the evolution of H_2 gas at Zn electrode. The cell reaction would be

$$Cu + 2H^+ \rightarrow Cu^{2+} + H_2 \qquad ...(7·6)$$

This shows that though the current can be withdrawn infinitesimally slowly when the opposing emf is infinitesimally smaller than the emf of the cell, but the chemical reactions cannot be reversed when the opposing emf greater than the emf of the cell is applied. This is evident from Eqs. (7·5) and (7·6) which are not opposite to one another. Hence this cell is an irreversible cell.

Measurement of EMF of Cells. When an electrochemical cell is in operation, the *emf of the cell does not remain strictly* constant due to concentration changes at the electrodes and other factors. Hence it is essential that emf of a cell should be measured at equilibrium conditions. The use of voltmeter to measure the emf is objectionable because when the voltmeter is connected to the cell a small current is drawn from the cell. It causes change in emf because the electrode reactions take place and the concentrations around the electrodes change. *Some reaction product may accumulate on the electrode causing a back emf called polarization.* Hence the emf measured by voltmeter will not, be the true emf of the cell.

These difficulties can be overcome if the emf is measured *when the circuit is open, i.e.*, when no current is allowed to flow from the cell. This can be done by balancing emf of the cell against the known emf of some other cell and obtaining equilibrium conditions using a **potentiometer.**

The principle involved can be understood by the set up as shown in Fig. 7·2, which is a schematic representation of a simple potentiometer. AB is a potentiometer slide wire made of a resistant metal. The wire should be of uniform cross section so that it has

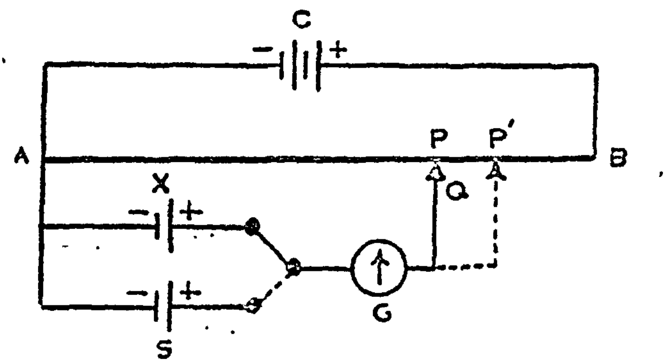

Fig. 7·2 Measurement of EMF of Cell by Potentiometer.

Reversible and Irreversible Cells. Thermodynamics finds its application in dealing with the change of chemical energy into electrical energy in the cell. Thermodynamic principles are applicable only to reversible reactions, hence it has become essential to distinguish between the reversible and irreversible cells. Recalling the thermodynamic conditions of reversibility of processes that a process is said to be **reversible** *if it is carried out in such a way that the driving force* is *only infinitesimally greater than the opposing force but if the opposing force is increased by an infinitesimal amount, the process can be reversed.* When these conditions are fulfilled by a cell, it is called a **reversible cell** otherwise it is an **irreversible cell.** Thus, if a reversible cell is connected to an *opposing force, i e ,* emf from an external source acting in opposite direction, which is infinitesimally lesser than the emf of the cell (*driving force*), than an infinitesimal amount of current will be given out and the chemical reaction will take place in one direction. If the applied emf is increased so that it becomes exactly equal to the emf of the cell, no current will flow and no chemical reaction will occur. If it is further increased so that it becomes greater than the emf of the cell by an *infinitesimal amount, the infinitesimal* small current will flow in opposite direction and the chemical reaction will also take place in the reverse direction.

As an illustration, let us connect Daniell cell to an external source of emf acting in opposite direction, which is infinitesimally smaller than the emf of the cell. The electrons will flow from zinc to copper electrode through the external circuit and the cell reaction will be

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

If the applied potential is increased so much that it becomes equal to the emf of the cell, no current will flow and no chemical reaction will occur. If the applied emf is further increased so that it becomes infinitesimally greater than the emf of the cell, the electrons will now flow from copper to zinc electrode through the external circuit and the cell reaction will be

$$Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$$

Thus, the direction of current and the direction of chemical change, both have reversed. Hence the Daniell cell is a reversible cell.

Now consider a cell composed of Zn and Cu electrodes immersed in dil H_2SO_4 solution. When the two electrodes are connected by a metallic wire, zinc dissolves with the evolution of H_2 at Cu electrode and electrons from Zn electrode will move to Cu electrode through the external circuit. The cell reaction is

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2(g) \qquad ...(7\cdot5)$$

If an external opposing emf infinitesimally smaller than that of the

cell is applied, an infinitesimal current will flow and the reaction will take place according to Eq. (7·5.) Now if the opposing emf is increased so that it becomes infinitesimally greater than the emf of the cell, the current flows in the opposite direction. Now Cu dissolves with the evolution of H_2 gas at Zn electrode. The cell reaction would be

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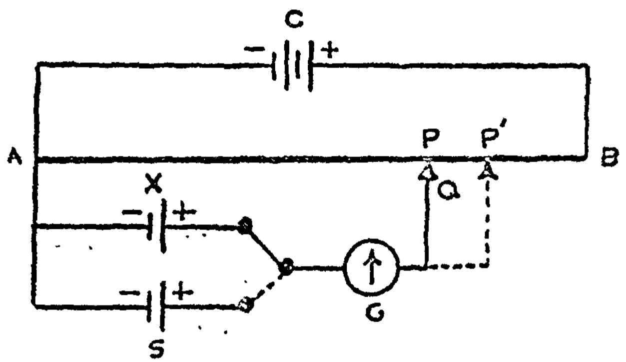

Fig. 7·2 Measurement of EMF of Cell by Potentiometer.

the same resistivity throughout its entire length. Hence the drop of potential along the length AB is proportional to its length. A storage battery C, having emf larger than the emf of the cell to be measured, is connected to the two ends of the wire A and B so that its potential is impressed across the resistance AB. Now one terminal of the cell X, whose emf is to be measured, is connected to A in such a way that its emf opposes the emf of C and the other terminal to the sliding contact Q, through a sensitive galvanometer G. By moving the sliding contact Q, a position P is found at which no current flows through the galvanometer. At this point, emf of the cell X just balances the drop of potential across AP due to the cell C. If $\mathcal{E}_x$ is the emf of the cell X then $\mathcal{E}_x$ will be proportional to the length AP of the wire.

Now the cell X is replaced by a standard cell S by means of a three-way key. The emf of the standard cell is known exactly. The sliding contact is readjusted to obtaine a point, say P′, when no current flows through the galvanometer. If $\mathcal{E}_s$ is the emf of the standard cell then $\mathcal{E}_s$ will be proportional to the length AP′ of the wire.

$$\text{Since } \mathcal{E}_x \propto \text{Length AP}$$

$$\text{and } \mathcal{E}_s \propto \text{Length AP}'$$

$$\therefore \quad \frac{\mathcal{E}_x}{\mathcal{E}_s} = \frac{\text{Length AP}}{\text{Length AP}'}$$

$$\text{or} \quad \mathcal{E}_x = \frac{\text{Length AP}}{\text{Length AP}'} \times \mathcal{E}_s \qquad \ldots(7{\cdot}7)$$

Thus, by measuring the lengths AP and AP′ and knowing the value of $\mathcal{E}_s$, the emf of the cell $\mathcal{E}_x$ can be evaluated.

The emf of standard cell plays an important role in the accurate determination of emf of any cell. Hence standard cell must have stable emf. The standard cell should have the following characteristics :

(*i*) Cell should give reproducible and constant emf which should not change with time.

(*ii*) Cell should be reversible.

(*iii*) Cell should not damage by a small passage of current through it.

(*iv*) Cell should have low temperature coefficient.

These characteristics are closely approximated by **Weston standard cell,** the usual form of which is shown in Fig. 7·3. It

consists of a H-shaped glass vessel, the side tubes of which are closed at their lower ends and Pt-wire fused at the bottom to make electric contact. One limb contains Hg covered with a paste of Hg_2SO_4 free from mercuric ions. This serves as positive electrode. The other limb contains a Cd-amalgam having 12 to 13% of Cd by weight. This serves as negative electrode. Some crystals of solid $CdSO_4 8/3H_2O$ are put over both the electrodes and the remaining vessel alongwith the connecting tube is filled with saturated solution of $CdSO_4$. A small air space is left over the solution in both the limbs for expansion and the upper ends are sealed. The cell reaction is

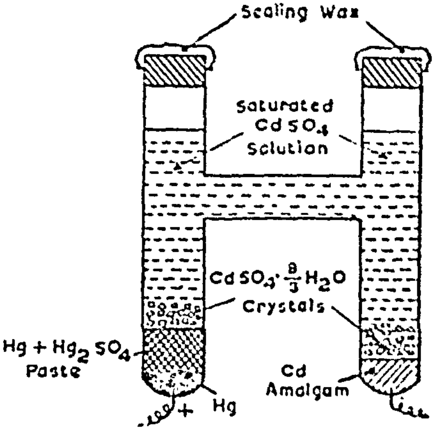

Fig. 7·3. The Weston Standard cell

$$Cd(s) + Hg_2SO_4(s) + \tfrac{8}{3}H_2O\ (l) = Cd\ SO_4\ \tfrac{8}{3}\ H_2O(s) + 2Hg\ (l)$$

The emf of this cell is 1·0183 volts at 20°C. and 1·01807 volts at 25°C.

Nernst Solution Pressure Theory. W. Nernst in 1889 suggested that all metals and hydrogen possess a property by virtue of which they tend to pass in solution as positive ions. This property, he called as **solution pressure.** If a metal, like Zn, when dipped in pure water tends to dissolve by virtue of its solution pressure and furnish a certain number of Zn^{2+} ions in water. Thus, the solution becomes positively charged due to the gain of Zn^{2+} ions and the metal which was, previously neutral, become negatively charged due to the loss of positive ions leaving behind electrons on the metal. The positive ions in the solution accumulated around the negatively charged electrode and thus a **electrical double layer** at the junction of metal and solution is set up. The electrical double layer grows up as more and more Zn^{2+} ions go in solution. This process will continue until so many Zn^{2+} ions are accumulated that the attraction of the opposite charges just stops the further expulsion of Zn^{2+} ions from the metal. On account of this electrostatic attraction, the amount of metal which pass into solution as ions is very small and hence the double layer is established rapidly. A potential of the electrode is due to the electrical double layer set up at the junction of metal and water.

is rather different. In this case, the positive ions of metal are already present in the solution which on account of their osmotic pressure in solution tends to resist the further entrance of positive metallic ions from the electrode. Now what happens in the solution will obviously depend on the relative values of solution pressure P of the metal and the osmotic pressure π of the solution containing metallic ions. In fact three cases as represented diagramatically in Fig. 7·4, are possible.

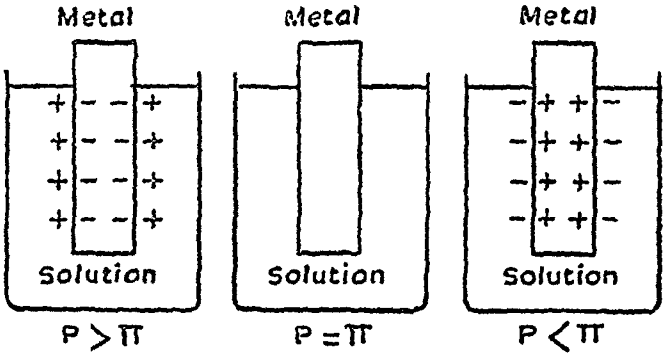

Fig. 7·4. Nernst Solution Pressure Theory

(*i*) *When* $P > \pi$. In this case, the *metal will continue to pass* in solution as positive ions until the accumulated positive charge in the solution prevents further passage of positive ions in the solution. The metal, therefore, becomes *negatively charged and the solution* becomes positively charged Mn, Zn, Cd and alkali metals are the examples of this case.

(*ii*) *When* $P < \pi$. The positive ions from the solution will deposit on the metal until the accumulated electrostatic charge prevent further action. In this case, the *metal becomes positively* charged and the solution acquires negative charge. Cu, Ag, Hg and Au behave in this manner.

(*iii*) *When* $P = \pi$. In this case no change occurs and hence no potential difference exists between the metal and solution. Such a system is known as **null electrode.**

Similar conclusions may be drawn for nonmetals like oxygen and halogens which pass into solution as their respective negative ions on account of their solution pressure.

Although Nernst solution pressure theory contributed much in the development of electrochemistry, the concept of so called solution pressure is now regarded as obsolete. According to the modern views, the electrode potential is regarded as dependent on the rates of the opposing processes–(*i*) passage of a metal or a nonmetal into solution in the form of ions and (*ii*) discharge of ions on the electrodes in the form of atoms of metal or nonmetal. The sign and

magnitude of the electrode potential depends on the relative rates of these processes. If the rate of passage of a metal into solution as ions is greater than the rate of deposition of ions on the metal, the metal electrode will acquire negative charge. On the other hand if the rate of passage of a metal into solution as ions is lesser than the rate of deposition of ions on the metal, the electrode will acquire positive charge. When the rates of opposing processes become equal, equilibrium is established and an electrical double layer is formed at the junction of the electrode and solution. This gives rise to electrode potential between the electrode and the solution.

Notations and Sign Conventions A galvanic cell is made up of two electrode system. For convenience, an electrochemical cell may be deposited with the help of chemical symbols of the electrodes and chemicals in the cell and using some conventions as given below :

(*i*) Boundaries between different phases or between solutions of different concentrations or compositions are depicted by putting a vertical line between them. For example, zinc in contact with zinc ions and two solutions of silver nitrate of different activities are represented as

$$Zn \mid Zn^{2+} \qquad AgNO_3(a_1) \mid AgNO_3(a_2)$$

(*ii*) Two vertical lines (‖) are drawn between the electrolytes when they are not in contact with each other directly and are connected by a salt bridge (discussed later on) to avoid liquid junction potential. For example a solution containing Zn^{++} ions separated from a solution containing Cd^{++} ions by a salt bridge is depicted as

$$Zn^{2+} \parallel Cd^{2+}$$

(*iii*) *In formulating a complete cell*, the anode half cell is written on the left hand side and the cathode half cell on the right hand side. The metal electrodes are always written on the outside extremes. For example, the formulation of Daniell cell is

$$Zn \mid Zn^{2+} \mid Cu^{2+} \mid Cu$$

(*iv*) To show that the left hand electrode is negative and the right hand electrode is positive, negative and positive signs may also be put on the anode and cathode respectively.

$$\overset{-}{Zn} \mid Zn^{2+} \mid Cu^{2+} \mid \overset{+}{Cu}$$

(*v*) The state of material, concentrations of solutions, pressures of gases are also indicated in the cell formulation by writing suitable signs within brackets as indicated in the following cell :

$$Pt \mid H_2(0{\cdot}9\ atm) \mid H^+(a=6) \parallel Ag^+(a=1) \mid Ag$$

(*vi*) The emf of the above formulated cell will have a p
value, This can be easily seen if we look to the changes ther

namically. If $\mathcal{E}$ is the emf of the cell, then the electrical work obtained from the reaction supplying $n\mathcal{F}$ coulombs of electricity will be given by $n\mathcal{F}\mathcal{E}$. The electrical work is obtained at the expense of free energy. For a reversible cell, the decrease in free energy will be equal to the electrical work, *i.e.*,

$$-\Delta G = n\mathcal{F}\mathcal{E} \qquad ...(7{\cdot}8)$$

We know that for a spontaneous reaction at constant pressure and temperature the free energy decreases and hence the value of ΔG will be negative. For example in the following cell

$$\overset{-}{Zn} \mid Zn^{2+}\ (a=1) \parallel Cd^{2+}\ (a=1) \mid \overset{+}{Cd}$$

the cell reaction is

$$Zn + Cd^{2+} = Zn^{2+} + Cd$$

In the cell formulated above, when the electrodes are joined by a wire, electrons spontaneously flow from anode to cathode showing that the cell reaction is spontaneous. Thus, the free energy of the cell reaction decreases and hence ΔG has negative value. From Eq. (7·8), it is evident that if ΔG has negative value $\mathcal{E}$ will have positive value.

The emf of the cell depends on temperature also; hence it should also be specified. For example, the emf of the above cell is 0·3590 volt at 25°C

If the above cell is formulated in the reverse order as

$$\overset{-}{Cd} \mid Cd^{2+}(a=1) \parallel Zn^{2+}(a=1) \mid \overset{+}{Zn}$$

the emf of this cell will be—0·3590 volt at 25°C. The cell reaction as given above will be spontaneous in the reverse direction and at least 0·3590 volt will have to be applied to the cell to make electrons flow from Cd to Zn electrode through the external circuit.

Chemical and Electrical Energy. The emf of a cell is a measure of the energy transferred for each coulomb of electricity which is caused to flow through the circuit. As already stated that if n faradays of electricity are obtained reversibly from a cell of emf $\mathcal{E}$, the total amount of electrical energy will be $n\mathcal{F}\mathcal{E}$. This is related to the decrease in free energy by the following relation

$$-\Delta G = n\mathcal{F}\mathcal{E} \qquad ...(7{\cdot}8)$$

This is different from the total amount of energy transferred in the reaction. It is the limiting amount of energy which is available for doing work. According to Eq. (4·70) Chapter 4, the emf of the cell $\mathcal{E}$ is related to the enthalpy change of the cell reaction by the relation

$$\mathcal{E} = \frac{-\Delta H}{n\mathcal{F}} + T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P \qquad ....(7{\cdot}9)$$

From this equation it is evident that if we know the value of $\mathcal{E}$ and its temperature coefficient $\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$ the value of $\triangle H$ can be evaluated. Further, we know that

$$\triangle G = \triangle H - T\triangle S$$

or $$-n\mathcal{F}\mathcal{E} = \triangle H - T\triangle S$$

or $$T\triangle S = \triangle H + n\mathcal{F}\mathcal{E}$$

$$= \triangle H + n\mathcal{F}\left[\frac{-\triangle H}{n\mathcal{F}} + T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P\right]$$

See notes

$$= \triangle H - \triangle H + n\mathcal{F}T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$$

or $$\triangle S = n\mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P \quad \ldots(7\cdot1$$

Thus, if we know the temperature coefficient, the change in entropy of the cell reaction can be calculated.

Example 1. *The emf of the cell*

$$Pt \mid H_2(1\ atm) \mid HCl \mid KCl \mid Hg_2Cl_2(s) \mid Hg$$

is 0·2676 volt at 25°C and its temperature coefficient is—0·0003[illegible] volt deg⁻¹. Calculate $\triangle H$, $\triangle S$ and $\triangle G$ for the reaction occurring in the cell.

Solution. The cell reaction is

$$Hg_2Cl_2(s) + H_2 \rightarrow 2Hg(l) + 2H^+ + 2Cl^-$$

(*i*) *Calculation of $\triangle H$.* We know that

$$\mathcal{E} = \frac{-\triangle H}{n\mathcal{F}} + T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$$

Here $\mathcal{E} = 0{\cdot}2676$ volt

$$\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P = -0{\cdot}000319 \text{ volt deg}^{-1}$$

$n = 2$

$\mathcal{F} = 96500$ coulombs

$T = 273 + 25 = 298°K$

$$\therefore \quad 0{\cdot}2676 = -\frac{\triangle H}{2\times 96500} + 298(-0{\cdot}000319)$$

or $$\triangle H = -(0{\cdot}2676 + 298\times 0{\cdot}000319)\times 2\times 96500$$

$$= -70490 \text{ volt coulomb deg}^{-1}$$

Since 1 cal = 4·184 volt coulomb

$$\therefore \quad \triangle H = -\frac{70490}{4{\cdot}184} = -16850 \text{ cal}$$

(*ii*) *Calculation of $\triangle S$.* We know that

$$\triangle S = n\mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$$

Here $n=2$

$\mathcal{F}=96500$ coulomb

$\left(\frac{\partial \mathcal{E}}{\partial T}\right)=-0.000319$ volt deg^{-1}

$\therefore \quad \Delta S=2\times 96500\times(-0.00319)$

$=-61.58$ volt coulombs deg^{-1}

$=-\frac{61.58}{4.184}=-14.72$ cal deg^{-1}.

(iii) Calculation of ΔG. We know that

$\Delta G=-n\mathcal{F}\mathcal{E}$

Here $n=2$

$\mathcal{F}=96300$ coulomb

$\mathcal{E}=0.2676$ volt

$\therefore \quad \Delta G=-2\times 96500\times 0.2676$

$=-51650$ volt coulomb deg^{-1}

$=-\frac{51650}{4.184}=-12340$ cal

Single Reversible Electrodes

A reversible cell is essentially composed of two reversible single electrodes. Various such single electrodes are known and they are divided chiefly into three types.

(1) **Electrodes Reversible to Cations.** These electrodes involve metal or hydrogen gas in contact with a solution containing their own ions. If M and M^{n+} reperesent the metal or its ion respectively, then the electrode may be represented as

$$M \mid M^{n+}$$

and the electrode reaction as

$$M \rightleftharpoons M^{n+}+ne^-$$

Examples of such type of electrodes are Zn in $ZnSO_4$ solution, Cu in $CuSO_4$ solution, Ag in $AgNO_3$ solution etc. The electrodes and the electrode reactions are given below.

Electrode	*Electrode Reacation*
$Zn \mid Zn^{2+}$	$Zn \rightleftharpoons Zn^{2+}+2e^-$
$Cu \mid Cu^{2+}$	$Cu \rightleftharpoons Cu^{2+}+2e^-$
$Ag \mid Ag^+$	$Ag \rightleftharpoons Ag^{+}+e^-$
$H^2 \mid H^+$	$\frac{1}{2}H^2 \rightleftharpoons H^{+}+e^-$

These electrodes are reversible to cations. The direction of flow of current through the cell determines the direction of reaction. Some metals which are attacked directly with water are used in the form of their mercury amalgam. For example, sodium electrode

$Na(Hg) \mid Na^+ \qquad\qquad Na \rightleftharpoons Na^{+}+e^-$

Among gas electrodes, hydrogen electrode is reversible to cations. In a gas electrode, a platinum foil coated with Pt-black is bubbled around the electrode. The gas is absorbed fully on the Pt-black surface. Platinum, thus, estableshes equilibrium between the gas and its ions and it used for making electric contacts. Thus in hydrogen electrode, hydrogsn gas is bubbled round the pt-foil

dipped in a solution containing H^+ ions. The electrode and the electrode reaction are given below.

$Pt \mid H_2(g) \mid H^+ \qquad \frac{1}{2} H_2 \rightleftharpoons H^+ + e^-$

(2) Electrodes Reversible to Anions These electrodes involve nonmetal in contact with their own ions (anions). If A represents a univalent nonmetal and A^- its anion, then the electrode and electrode reactions are

$Pt \mid A^- \mid A \qquad A^- \rightleftharpoons A + e^-$

since nonmetals are not electrical conductors, generally Pt is used, as discussed above, as a type of electrode is chlorine electrode :

$Pt \mid Cl^- \mid Cl_2 \qquad Cl^+ \rightleftharpoons \frac{1}{2} Cl_2 + e^-$

Most frequently used electrodes reversible to anions are.

Metal-Insoluble Salt Electrodes. These electrodes consist of a metal and its sparingly soluble salt in contact with a solution having the same anion. Examples of such electrodes are

Electrode	*Electrode Reaction*
$Ag \mid AgCl(s) \mid HCl$ soln	$Ag(s) + Cl^- \rightleftharpoons AgCl(s) + e^-$
$Hg \mid Hg_2Cl_2(s) \mid KCl$ soln	$2Hg_2 + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^-$

These electrodes are reversible with respect to common anion.

(*iii*) Oxidation-Reduction (Redox) Electrodes. These electrodes consist of unattackable metal, such as platinum, dipped in a solution having oxidised and reduced states of an oxidation-reduction system. For example a platinum wire dipped in a solution containing Fe^{2+} and Fe^{3+} ions, or $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions or Sn^{2+} and Sn^{4+} ions or quinhydrone *i. e.*, hydroquinone and quinone together with hydrogen ions, constitute redox electrodes. The electrodes and the electrode reactions are

Electrode	*Electrode Reaction*
$Pt \mid Fe^{2+}\ Fe^{3+}$	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$
$Pt \mid Sn^{2+}, Sn^{4+}$	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$
$Pt \mid Fe(CN)_6^{4-}, Fe(CN)_6^{3-}$	$Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^-$
$Pt \mid$ quinhydrone	$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^+ + 2e^-$

Since the electrodes have oxidised and reduced forms in equilibrium, they are also called **oxidation-reduction** or **redox electrodes.** The unattackable metal acts as conductor of electrons and is also used for making electric contacts. There electrodes can behave reversibly only when both the oxidised and reduced states of the system are present in the solution.

All these types of reversible electrodes, though structurally different, are based on the same fundamental principle that electrons are either liberated or taken up reversibly. Thus, all reversible electrodes involve oxidised and reduced states and the electrode reaction may be represented in the following general form.

Reduced State $\rightleftharpoons$ *Oxidised State* $+ne^-$ ...

where n is the numbers of electrons involved.

The Nernst Equation. The emf of a cell depends concentrations or more accurately on the activities of the sub involved in the cell reaction. From rigorous thermodynam derations using free energy concept, a general exp n for of the cell in terms of activities of reactants uct

obtained. The thermodynamic derivation is beyond the scope of this book. For the following general cell reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

the emf of the cell, $\mathcal{E}$, is given by

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{(a_\mathrm{C})^c \times (a_\mathrm{D})^d}{(a_\mathrm{A})^a \times (a_\mathrm{B})^b} \qquad ...(7{\cdot}12)$$

where $\mathcal{E}^\circ$ is known as **standard emf** or **standard cell potential,** n is the number of electrons transferred in the reaction as written, $\mathcal{F}$ is the faraday, T is the temperature of the cell in degrees absolute, R is the gas constant, a_A, a_B, a_C and a_D are the activities of A, B, C, and D, respectively in the reversible cell. This expression is known as **Nernst equation.**

Eq. (7·12) can be written as

$$\mathcal{E} = \mathcal{E}^\circ - \frac{2{\cdot}203\ RT}{n\mathcal{F}} \log_{10} \frac{(a_\mathrm{C})^c\ (c_\mathrm{D})^d}{(a_\mathrm{A})^a\ (a_\mathrm{B})^b} \qquad ...(7{\cdot}13)$$

At 25°C, the value of

$$\frac{2{\cdot}303\ RT}{\mathcal{F}} = \frac{2{\cdot}203 \times 8{\cdot}32 \times 298}{96500} = 0{\cdot}0591$$

Hence at 25°C., Eq. (7·13) can be written as

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0{\cdot}0591}{n} \log_{10} \frac{(a_\mathrm{C})^c\ (a_\mathrm{D})^d}{(a_\mathrm{A})^a\ (a_\mathrm{B})^b} \qquad ...(7{\cdot}14)$$

If the reactions and the products are in their standard state, *i.e.*, at unit activity, Eq. (7·14) reduces to

$$\mathcal{E} = \mathcal{E}^\circ$$

Hence $\mathcal{E}^\circ$, the **standard cell potential** is defined as *the em f of the cell when the reactants and the products of the cell reaction are at unit activity.*

To illustrate the use of Eq. (7·12), consider the Daniell cell

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \parallel \mathrm{Cu}^{2+} \mid \mathrm{Cu}$$

The cell reaction is given by the following equation

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Zn}^{2+} + \mathrm{Cu}$$

The cell reaction involves the transfer of 2 electrons, hence $n=2$ Applying Eq. (7·12) to this cell reaction

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0{\cdot}0591}{2} \log_{10} \frac{a_{\mathrm{Zn}^{+2}} \times a_\mathrm{Cu}}{a_\mathrm{Zn} \times a_{\mathrm{Cu}^{2+}}} \qquad ...(7{\cdot}15)$$

The activity of a substance in solid state is taken equal to unity, hence $a_\mathrm{Cu} = 1$ and $a_\mathrm{Zn} = 1$. Thus, Eq. (7·15) reduces to

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0{\cdot}0591}{2} \log_{10} \frac{a_{\mathrm{Zn}^{2+}}}{a_{\mathrm{Cu}^{2+}}} \qquad ...(7{\cdot}16)$$

from this equation it is evident that the emf of the cell depends on the activities of Cu^{++} and Zn^{++} ions in their solutions.

Example 2. *Calculate the emf of the following cell at 25°C.*

$$Zn \mid Zn^{2+}\ (a = 0{\cdot}01)\ \|\ Cu^{2+}\ (a = 0{\cdot}1) \mid Cu$$

The standard emf of the cell is 1·0988 volt at 25°C.

Solution. The cell reaction is

$$Zn + Cu^{2+} = Zn^{2+} + Cu$$

We know that at 25° C,

$$\mathcal{E} = \mathcal{E}^o - \frac{0{\cdot}0591}{n} \log_{10} \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

Here $\mathcal{E}^o = 1{\cdot}0988$ volt

$$a_{Cu^{+2}} = 0{\cdot}1$$

$$a_{Zn^{2+}} = 0{\cdot}01$$

$$n = 2$$

$$\therefore \quad \mathcal{E} = 1{\cdot}0988 - \frac{0{\cdot}0591}{2} \log \frac{0{\cdot}1}{0{\cdot}01}$$

$$\mathcal{E} = 1{\cdot}0988 + 0{\cdot}02955 = \text{[illegible] volt}$$

Single Electrode Potentials. A complete cell is a combination of two half and the emf of the cell is the resultant potential difference between the electrodes forming the cell. The emf of the cell can be measured directly but the direct determination of potential of an electrode is not possible. This difficulty has been overcome by defining the electrode potentials with respect to the potential of an electrode chosen as reference. Thus, the potential of the reference electrode can be employed as the basis for the determination of potentials of all other electrodes. A universally used reference electrode for this purpose is the **standard hydrogen electrode** or **normal hydrogen electrode** in which H_2 gas is at 1 atm pressure and the activity of H^+ ions in the solution is unity. The cell is represented as

$$Pt \mid H_2\ (1\ \text{atm}) \mid H^+\ (a = 1)$$

The electrode potential of this electrode is taken, quite arbitrarily, as *zero.* Thus, if an electrode whose electrode potential is to be determined, is coupled with standard hydrogen electrode, the emf of the cell will give the value of the potential of the electrode.

Suppose an electrode, say $M \mid M^{n+}$ is coupled with standard hydrogen electrode to give the following cell

$$M \mid M^{n+}\ \text{soln} \mid H^+\ (a = 1) \mid H_2\ (1\ \text{atm}) \mid Pt$$

The emf of the cell will be equal to the potential $\mathcal{E}$ of the electrode $M \mid M^{n+}$. The electrode potentials based on the zero value of standard hydrogen electrode are referred to as **hydrogen scale.** The half cell reactions of the electrodes of the above cell are as follo

Left hand electrode	$M \rightleftharpoons M^{n+} +$
Right hand electrode	$nH^+ + ne^- \rightleftharpoons \frac{1}{2}n\ H$
The overall cell reaction	$M + nH^+ \rightleftharpoons M^{n+}$

Using Eq. (7·12), the emf of this cell is given by

$$\mathcal{E} = \mathcal{E}^{o} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{M^{n+}} \times (a_{H_2})^{n/2}}{a_M \times (a_{H^+})^n} \qquad ...(7{\cdot}20)$$

In the standard hydrogen electrode, the pressure of H_2 gas is 1 atm, hence $a_{H_2} = 1$. Further, the activity of H^+ ions in solution is also unity. Since the potential of standard hydrogen electrode is taken as zero, the emf of the cell represents the potential of the left hand electrode. Hence Eq. (7·20) may be written as

$$\mathcal{E}_{el} = \mathcal{E}^{o}_{el} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{M^{n+}}}{a_M} \qquad ...(7{\cdot}21)$$

where $\mathcal{E}_{el}$ and $\mathcal{E}^{o}_{el}$ represent the electrode potential and standard electrode potential of left hand electrode respectively. Since M represents the reduced state and M^{n+} the oxidised state, Eq. (7·21) may be generalized as

$$\mathcal{E}_{el} = \mathcal{E}^{o}_{el} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{ox}}{a_{red}} \qquad ...(7{\cdot}22)$$

where a_{ox} and a_{red} are the activities of a substance in the oxidised and the reduced states respectively. Since the left hand electrode reaction, Eq (7·17), is an oxidation reaction, $\mathcal{E}_{el}$ is called **oxidation potential** and $\mathcal{E}^{o}_{el}$ is called **standard oxidation potential** *i.e.*, the potential of the electrode when oxidised and reduced states are at unit activity.

The electrode potentials with reference to standard hydrogen electrode may be **positive** or **negative.** The **positive** value shows that the electrode reaction, vide Eq. (7·17) is spontaneous and thus the electrode is negative with respect to the reference standard hydrogen electrode and supplies electrons to the external circuit. The **negative** value shows the reverse of the electrode reaction, vide Eq. (7·17), is spontaneous and thus, the electrode becomes positive with respect to hydrogen electrode. In this case, hydrogen electrode will supply electrons to the external circuit.

Let us now deduce expression for different types of simple single electrodes :

Electrodes Reversible to Cations. For example, we take copper in copper sulphate solution. The electrode and the oxidation reaction are

$$Cu \mid Cu^{2+} \qquad Cu \rightleftharpoons Cu^{2+} + 2e^-$$

Utilizing Eq. (7·22), we can write

$$\mathcal{E}_{Cu} = \mathcal{E}^{o}_{Cu} - \frac{RT}{2\mathcal{F}} \ln \frac{a_{Cu^{2+}}}{a_{Cu}} \qquad ...(7{\cdot}23)$$

Since a_{Cu}, the activity of solid copper is unity, Eq. (7·21) reduces to

$$\mathcal{E}_{Cu} = \mathcal{E}^{o}_{Cu} - \frac{RT}{2\mathcal{F}} \ln a_{Cu^{2+}} \qquad ...(7{\cdot}24)$$

Thus, the electrode potential depends on standard oxidation potential of copper $\mathcal{E}^o_{Cu}$ and the activity of Cu^{2+} ions.

(2) **Electrodes Reversible to Anions.** For example, we take chlorine electrode in which chlorine at 1 atm pressure and is in contact with its own anion. The electrode and the oxidation reactions are

$$(Pt\text{-}I_r) \mid Cl_2\ (1\ \text{atm}) \mid Cl^- \qquad Cl^- = \tfrac{1}{2}\, Cl_2 + e^-$$

Utilizing Eq. (7·22), we can write

$$\mathcal{E}_{Cl_2} = \mathcal{E}^o{}_{Cl_2} - \frac{RT}{\mathcal{F}} \ln \frac{(a_{Cl})^{\frac{1}{2}}}{a_{Cl^-}} \qquad ...(7{\cdot}25)$$

Since Cl_2 gas is at 1 atm. $a_{Cl_2} = 1$, Eq. (7·25) reduces to

$$\mathcal{E}_{Cl_2} = \mathcal{E}^o{}_{Cl_2} - \frac{RT}{\mathcal{F}} \ln \frac{1}{a_{Cl^-}}$$

or

$$\mathcal{E}_{Cl_2} = \mathcal{E}^o{}_{Cl_2} + \frac{RT}{\mathcal{F}} \ln a_{Cl^-} \qquad ...(7{\cdot}26)$$

(*iii*) **Oxidation-Reduction or Redox Electrodes.** For example, we take stannic-stannous system. The electrode and the oxidation reaction are

$$Pt \mid Sn^{2+}, Sn^{4+} \quad Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$$

Utilizing Eq. (7·22) we can write

$$\mathcal{E}_{\text{redox}} = \mathcal{E}^o{}_{\text{redox}} - \frac{RT}{2\mathcal{F}} \ln \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}} \qquad ...(7{\cdot}27)$$

Thus, the potential of the electrode depends on the activities of Sn^{4+} and Sn^{2+} ions in the solution.

Now it is clear that if we know the oxidation process at an electrode, the expression for its electrode potential can be easily derived. The electrode potentials thus obtained are **oxidation potential** of the electrode. The **reduction potential** of the electrode is numerically equal to its oxidation potential but with the sign reversed. A galvanic cell is a combination of two electrodes. If the cell is represented by the conventions described earlier, the oxidation occurs at the left hand electrode and the reduction occurs at the right hand electrode. The oxidation potential, of both the electrodes can be obtained utilizing Eq. (7·22). The corresponding reduction potential of the right hand electrode can be obtained by simply reversing the sign of its oxidation potential. *The* **emf of the complete cell** *is equal to the algebraic sum of oxidation potential of the left hand electrode and the reduction potential of the right hand electrode.* If only oxidation potentials are considered, then the emf of the cell will be equal to the *difference of oxidation potentials of the two electrodes.*

Standard Electrode Potential. From Eq. (7·22), it is evident that when the oxidised state and the reduced state are at unit activity, the **electrode potential** $\mathcal{E}$ becomes equal to the **Standard electrode potential** $\mathcal{E}^o$. Under standard condition, the values of $\mathcal{E}^o$ for different electrode systems are constant. Hence the standard electrode potential is a definite property of the electrode system. The standard oxidation potentials of some electrodes at 25°C together with their oxidation reactions are given in the Table 7 1.

Table 7·1

Standard Oxidation Potentials at 25°C

Electrode	*Electrode Reaction (oxidation)*	$\mathcal{E}^o$ *(volts)*
Li | Li^+	Li (s) → $Li^+ + e^-$	+3·045
K | K^+	K(s) → $K^+ + e^-$	+2·9241
Ca | Ca^{2+}	Ca (s) → $Ca^{2+} + 2e^-$	+2·87
Na | Na^+	Na (s) → $Na^+ + e^-$	+2·7146
Zn | Zn^{2+}	Zn (s) → $Zn^{2+} + 2e^-$	+0·7618
Fe | Fe^{2+}	Fe (s) → $Fe^{2+} + 2e^-$	+0·441
Cd | Cd^{2+}	Cd (s) → $Cd^{3+} + 2e^-$	+0·403
Pb | $PbSO_4$ (s) | SO_4^{2-}	Pb (s) + SO_4^{2-} → Pb SO_4 (s) + $2e^-$	+0·3546
Ni | Ni^{2+}	Ni (s) → $Ni^{2+} + 2e$	+0·236
Ag | Ag I (s) | I^-	Ag (s) + I^- → AgI (s) + e^-	+0·1522
Sn | Sn^{2+}	Sn (s) → $Sn^{2+} + 2e$	+0·140
Pb | Pb^{2+}	Pb (s) → $Pb^{2+} + 2e^-$	+0·1265
Pt | H_2 | H^+	$\frac{1}{2}H_2$ (g) → $H^+ + e^-$	Zero
Ag | Ag Br (s) | Br^-	Ag (s) Br^- → Ag Br (s) + e^-	−0·0711
Pt | Sn^{2+}, Sn^{4+}	Sn^{2+} → $Sn^{4+} + 2e^-$	−0·14
Ag | Ag Cl (s) | Cl^-	Ag (s) + Cl^- → Ag Cl (s) + e^-	−0·2225
Hg | Hg_2 Cl_2 (s) | Cl^-	2Hg (s) + $2Cl^-$ → $2Hg_2$ Cl_2 + $2e^-$	−0·2680
Cu | Cu^{2+}	Cu → $Cu^{2+} + 2e^-$	−0·337
Pt | I_2 | I^-	I^- → $\frac{1}{2}$ $I_2 + e^-$	−0·5355
Hg | Hg_2 SO_4(s) | SO_4^{2-}	$\frac{1}{2}$Hg(l) + SO_4^{2-} → Hg_2SO_4 (s) + $2e^-$	−0·6141
Pt | Fe^{2+}, Fe^{3+}	Fe^{2+} → $Fe^{3+} e^-$	−0·771
Ag | Ag^+	Ag (s) → $Ag^+ + e^-$	−0·7991
Pt | Br_2 (l) | Br^-	Br^- → $\frac{1}{2}$ $Br_2 + e^-$	−1·2652
Pt | Cl_2 (g) | Cl^-	Cl^- → $\frac{1}{2}$ $Cl_2 + e^-$	−1·3595
Pt | Ce^{3+}, Ce^4	Ce^{3+} → $Ce^{4+} + e^-$	−1·61

The standard oxidation potential of an electrode shows the tendency of the electrode to deliver electrons to the *external circuit* in $\mathcal{E}^o$ shows that the oxidation process is spontaneous at the electrode and the electrode gives out electrons to the external circuit. A negative value of $\mathcal{E}^o$ indicates the reverse behaviour. *i.e.*, the reduction process is spontaneous at the electrode and the electrons are absorbed from the external circuit. The tendency of electrodes to lose electorns

is the measure of its oxidising strength. If the electrode has greater tendency to release electrons, it is powerful reducing agent. Similarly if an electrode has more tendency to gain electrons, it is powerful oxidising agent. Thus, the table gives a quatitative comparison of the strenghts of oxidising and reducing agents.

It is evident from the table that the metals near the top of the table are strong reducing agents and their ions are stable. The elements near the bottom of the table are comparatively stable metals and their ions are easily reducible to the metals. Hence any metal can reduce any cation below it in the table from its molar solution. For example

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Zn being higher in the table than Cu reduces Cu^{2+} ions into Cu metal in its molar solution.

Table 7·1 gives the standard oxidation potentials. The corresponding standard reduction potentials, involving the reverse electrode reaction can be obtained by reversing the sign of the oxidation potentials. Thus, for the cadmium electrode

$$Cd \mid Cd^{2+} \quad Cd^{-} \rightarrow Cd^{2+} + 2e^{-} \quad \mathcal{E}^{o}_{ox} = +0{\cdot}403 \text{ volt}$$
$$Cd^{2+} \mid Cd \quad Cd^{2+} - 2e^{-} \rightarrow Cd \quad \mathcal{E}^{o}_{red} = -0{\cdot}403 \text{ volt}$$

In case of silver-silver chloride electrode,

$$Ag \mid Ag\,Cl\,(s)\,Cl \quad Ag + Cl^{-} \rightarrow Ag\,Cl + e^{-} \quad \mathcal{E}^{o}_{ox} = -0{\cdot}2225 \text{ volt}$$
$$Cl^{-} \mid Ag\,Cl\,(s)\,Ag \quad Ag\,Cl + e^{-} \rightarrow Ag + Cl^{-} \quad \mathcal{E}^{o}_{red} = +0.2225 \text{ volt}$$

Eq. (7·22) is for oxidation electrode process and can be written as

$$\mathcal{E}^{o'}_{ox} = \mathcal{E}^{o}_{ox} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{ox}}{a_{red}} \qquad \ldots(7{\cdot}28)$$

The expression for reduction electrode potential can be obtained from the above equation by reversing the sign. Thus,

$$-\mathcal{E}_{ox} = -\mathcal{E}^{o}_{ox} + \frac{RT}{n\mathcal{F}} \ln \frac{a_{ox}}{a_{red}}$$

or
$$\mathcal{E}_{red} = \mathcal{E}^{o}_{red} + \frac{RT}{n\mathcal{F}} \ln \frac{a_{ox}}{a_{red}} \qquad \ldots(7{\cdot}29)$$

Example 3. *Calculate the oxidation potential of zinc electrode when a Zn-rod is immersed in a solution of zinc sulphate in which the activity of Zn^{++} ions is 0·15. The standard electrode potential of zinc electrode is 0·7618 volt.*

Solution. The electrode may be represented as

$$Zn \mid Zn^{2+} \; (a = 0{\cdot}15)$$

This electrode is reversible to cations. We know that for th[illegible]

the given by

$$\mathcal{E}_{Zn} = \mathcal{E}^{o}{}_{Zn} - \frac{RT}{2\mathfrak{F}} \ln a_{Zn^{2+}} = \mathcal{E}^{o}{}_{Zn} - \frac{2{\cdot}303\ RT}{2\mathfrak{F}} \log_{10} a_{Zn^{2+}}$$

Here $\mathcal{E}^{o}{}_{Zn} = 0{\cdot}7618$ volt

$a_{Zn^{2+}} = 0{\cdot}15$

and at 25°C $\frac{2{\cdot}303\ RT}{\mathfrak{F}} = 0{\cdot}0591$

$$\therefore \quad \mathcal{E}_{Zn} = 0{\cdot}7618 - \frac{0{\cdot}0591}{2} \log_{10} (0{\cdot}15)$$

$$= 0{,}7618 + 0{\cdot}244$$

$$= 0{\cdot}7862 \text{ volt}$$

+0.024

Example 4. *Calculate the oxidation potential of the following electrode at 25°C.*

$$Ag \mid Ag\,Br\,(s) \mid Br^{-}(a = 0{\cdot}2)$$

The Standard potential of this electrode is —0·0711 volt at 25°C.

Solution. The electrode is reversible to anions. For this electrode, we know that

$$\mathcal{E} = \mathcal{E}^{o} - \frac{RT}{\mathfrak{F}} \ln \frac{1}{a_{\cancel{Cl^-}}} = \mathcal{E}^{o}{}_{Cl^-} - \frac{2{\cdot}303\ RT}{\mathfrak{F}} \log_{10} \frac{1}{a_{\cancel{Cl^-}}}$$

/ Br / Br

Here $\mathcal{E}^{o} = -0{\cdot}0711$ volt

$a_{Cl^-} = 0{\cdot}2$

at 25°C $2{\cdot}303\ RT/\mathfrak{F} = 0{\cdot}0591$

$$\therefore \quad \mathcal{E} = -0{\cdot}0711 + 0{\cdot}0591 \log_{10} 0{\cdot}2$$

$-0.0711 + (0.0591)(\bar{1}.30b)$ $= -0{\cdot}0711 - 0{\cdot}0113$

$-0.0711 - (0.0591)(0.6990)$ $= 0{\cdot}1124$ volt. (−)

.7
−.06
.04

Example 5. *Determine the oxidation potential of a redox electrode consisting a platinum wire immersed in a solution containing stannous and stannic ions at activities of 0 030 and 0·015 respectively at 25°C. The standard oxidation potential of this electrode is —0 14 volt.*

Solution. For such electrode, we know that

$$\mathcal{E}_{redox} = \mathcal{E}^{o}{}_{redox} - \frac{RT}{2\mathfrak{F}} \ln \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}}$$

$$= \mathcal{E}^{o}{}_{redox} - \frac{2{\cdot}303\ RT}{2\mathfrak{F}} \log_{10} \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}}$$

Here $\mathcal{E}^{o}{}_{redox} = -1{\cdot}14$ volt

$a_{Sn^{4+}} = 0{\cdot}030$

$a_{Sn^{2+}} = 0{\cdot}015$

at 25°C $\frac{2.303\ RT}{\mathcal{F}} = 0.0591$

$$\therefore \qquad \mathcal{E}_{redox} = -0.14 - \frac{0.0591}{2} \log_{10} \frac{0.030}{0.150}$$
$$= -0.14 + 0.0206$$
$$= -0.1194 \text{ volt.}$$

Reference Electrodes. To measure the potential of an electrode, it is essential that the electrode should be combined with some other electrode known as **reference electrode** whose potential is known. The electrode potential will be equal to the difference of the emf of complete cell and the potential of reference electrode. We have already discussed the use of *standard hydrogen electrode* whose potential is arbitrarily fixed as zero, as the reference electrode. Electrodes other than standard hydrogen electrodes are also used as reference electrodes. We shall now discuss some commonly used reference electrodes.

(1) **Hydrogen Electrode.** The hydrogen electrode usually consists of a platinized platinum foil immersed in a solution containing H^+ ions. Pure hydrogen gas at 1 atm is bubbled through the solution. The Pt foil should be immersed in the solution in such a way that about half of its area remains in the solution and the rest in the gas phase. Hydrogen gas is absorbed fully on the platinum black and the equilibrium between the gas and its ions is established on Pt-foil which also acts as electric contact for the electrode. Out of several forms of hydrogen electrode, one is shown in Fig. 7·5.

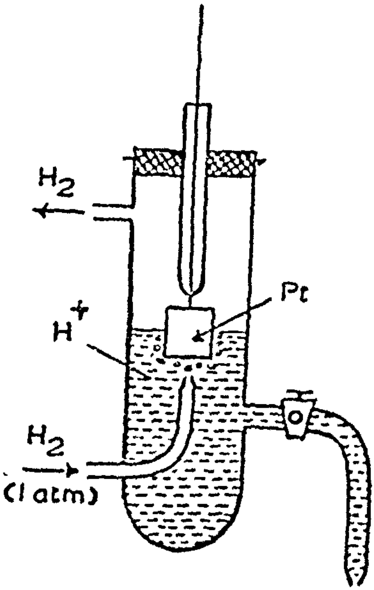

Fig. 7·5 Hydrogen Electrode

The electrode and the electrode oxidation reaction are

$$\text{Pt} \mid H_2 \text{ (1 atm)} \mid H^+(a)$$
$$\tfrac{1}{2}H_2 \rightleftharpoons H^+ + e^-$$

The potential of the electrode is given by

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{\mathcal{F}} \ln a_{H^+}$$

$$= -\frac{RT}{\mathcal{F}} \ln a_{H^+} \qquad ..(7{\cdot}30)$$

because, $\mathcal{E}°$ will be equal to zero by definition. Thus, the potntial of this electrode depends on the activity of H^+ ions in the solution. If H^+ ions in the solution are at unit activity, the electrode becomes standard hydrogen electrode and the value of electrode potential will be zero according to Eq. (7 30). It should be noted that if a_{H^+} is not unity, the potential of hydrogen electrode will not be equal to zero

For correct measurement of potential of any electrode using standard hydrogen electrode, it is essential that hydrogen and *platinum surface* should be highly pure. Great experimental difficulties are faced in maintaining the pressure of the gas at 1 atm and H^+ ions at unit activity in the solution. It is for this reason that other secondary reference electrodes have been devised which are less capricious and have accurately known electrode potentials.

(2) **Calomel Electrode.** The calomel electrode consists of mercury in contact with potassium chloride solution saturated with mercurous chloride. The cell is represented as

$$Hg \mid Hg_2\,Cl_2(s) \mid KCl \text{ soln.}$$

The oxidation reaction is

$$2\,Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

The electrode is reversible with anion, the electrode potential is given by

$$\mathcal{E}_{cal} = \mathcal{E}°_{cal} + \frac{RT}{2\mathcal{F}} \ln a^2_{Cl^-} = \mathcal{E}° + \frac{RT}{\mathcal{F}} \ln a_{Cl^-} \qquad ...(7{\cdot}31)$$

This shows that the electrode potential depends on the activity of Cl^- ions and hence on the concentration of KCl solution used. Three types of calomel electrodes depending on the concentration of KCl solution are in common use. The concentrations of KCl solution used are **0·1** N, **1·0** N, and **saturated** and the corresponding electrodes are called **decinormal, normal** and **saturated calomel electrodes.** Their electrode potentials against standard hydrogen electrodes have been accurately determined. The electrodes and their oxidation potential at 25°C are

$$Hg \mid Hg_2Cl_2\,(s) \mid KCl\,(0{\cdot}1N) \qquad \mathcal{E}_{cal} = -0{\cdot}3338 \text{ volt}$$

$$Hg \mid Hg_2Cl_2\,(s) \mid KCl\,(1{\cdot}0N) \qquad \mathcal{E}_{cal} = -0{\cdot}280 \text{ volt}$$

$$\therefore \quad Hg \mid Hg_2Cl_2\,(s) \mid KCl \text{ (satd. soln.)} \qquad \mathcal{E}_{cal} = -0{\cdot}2415 \text{ volt.}$$

A common form of calom elelectrode is shown in Fig. 7·6. A small amount of pure mercury is placed at the bottom of the tube as shown in the figure. The mercury is covered with a paste of Hg_2Cl_2 (calomel), Hg and KCl solution. The vessel is then filled with a solution KCl of appropriate strength saturated with $Hg_2 Cl_2$. A Pt-wire sealed in glass tube with a little portion exposed is dipped in Hg at the bottom to make electrical contacts.

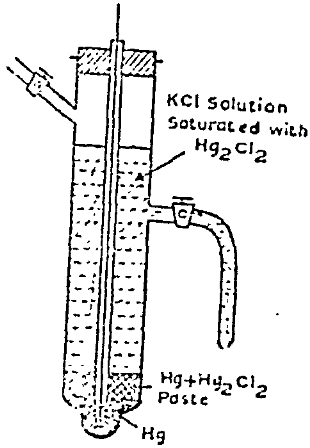

Fig. 7·6 Calomel Electrode.

(3) Silver-Silver Chloride Electrode. Because of the toxic nature of mercury, silver-silver chloride electrode is widely used these days. This electrode is analogous to the calomel electrode. It consists of a silver wire coated with silver chloride layer and immersed in a solution containing Cl^- ions. The electrode is represented as

$$Ag \mid Ag\,Cl\,(s) \mid Cl^-\,(a)$$

The oxidation reaction is

$$Ag(s)+Cl^- \rightleftharpoons Ag\,Cl(s)+e^-$$

The electrode is reversible to Cl^- ions and the electrode potential is given by

$$\mathcal{E}_{Ag\text{-}AgCl}=\mathcal{E}^{o}_{Ag\text{-}AgCl}+\frac{RT}{\mathcal{F}}\ln a\,cl^- \qquad ...(7{\cdot}32)$$

The electrode potential of this electrode depends on the activity of Cl^- ions. The electrode potential of the following Ag—AgCl electrodes at 25°C are

$Ag \mid HgCl\,(s) \mid Cl^-\,(a=1)$ $\quad \mathcal{E}_{Ag—AgCl} = —0{\cdot}2225$ volt

$Ag \mid AgCl\,(s) \mid Cl^-$ (saturated) $\quad \mathcal{E}_{Ag—AgCl} = —0{\cdot}197$ volt

Concentration Cells

In the cells so far considered, the emf is produced due to chemical reactions occurring in the cell. There is another type of cells, known as **concentration cells**, in which the emf arises due to the reversible transfer of matter from one region of the cell to another. The substances are present at different concentrations or activities in different regions of the cell. Chemical reactions, of course, occur at different electrodes but they are such that the chemical change occurring in one half cell is exactily balanced by the reverse chemical change occurring in the other half cell resul-

ting no net chemical change in the cell. The net process is, therefore, a purely physical change involving the levelling of the concentration differences between different points of the cell. These concentration cells may be divided into two types :

(i) Electrode concentration cells, and

(ii) Electrolyte concentration cell.

(1) Electrode Concentration Cells

In these cells, the electrodes of the same material but at different concentrations or activities are immersed in the same solution of an electrolyte containing the ions of the electrode. Amalgam electrodes and gaseous electrodes are of this type. Consider two amalgams of silver at different activities a_1 and a_2 are in contact with a silver nitrate solution. The cell may be represented as

$$\underset{a_1}{Ag\,(Hg)} \mid AgNO_3 \text{ soln} \mid \underset{a_2}{Ag(Hg)}$$

where $a_1 > a_2$, The electrode reactions are

At left hand electrode $Ag(a_1) \rightleftharpoons Ag^+ + e^-$

At right hand electrode $Ag^+ + e^- \rightleftharpoons Ag(a_2)$

The overall cell reaction $Ag(a_1) \rightleftharpoons Ag(a_2)$ ...(7·33)

Hence, the net cell reaction involves no chemical change but involves only the transfer of silver at one activity another activity. Utilizing Eq. (7·12) the emf of such cell is given by

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} \qquad \text{...(7·34)}$$

For such cells, $\mathcal{E}^\circ$ is necessarily equal to zero because when $a_1 = 1$ and $a_2 = 1$, the two electrode systems will become identical and hence no current will flow. Thus, Eq. (7·34) reduces to

$$\mathcal{E} = -\frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1}$$

or $$\mathcal{E} = \frac{RT}{\mathcal{F}} \ln \frac{a_1}{a_2} \qquad \text{...(7·35)}$$

A gaseous electrode concentration cell, for example, two hydrogen electrodes in which H_2 gas is passed at two different pressures P_1 and P_2 may be represented as

$$Pt \mid H_2\,(P_1) \mid HCl \text{ soln.} \mid H_2(P_2) \mid Pt$$

where $P_1 > P_2$. The overall cell reaction is

$$H_2(P_1) \rightleftharpoons H_2\,(P_2)$$

The emf of this cell is given by

$$\mathcal{E} = \frac{RT}{\mathcal{F}} \ln \frac{P_1}{P_2} \qquad \text{...(7·36)}$$

Example 6. *Calculate the potential of the following concentration cell at 25°C.*

$$\underset{(a=1)}{Cd(Hg)} \mid CdSO_4\ solu \mid \underset{(a=0\cdot1)}{Cd(Hg)}$$

Solution. For such cell, we know that

$$\mathcal{E} = \frac{RT}{n\mathfrak{F}} \ln \frac{a_1}{a_2} = \frac{2\cdot303\ RT}{n\mathfrak{F}} \log_{10} \frac{a_1}{a_2}$$

At 25°C, the value of $\dfrac{2\cdot303\ RT}{\mathfrak{F}} = 0\cdot0591$

$$\therefore \qquad \mathfrak{F} = \frac{0\cdot0591}{n} \ln g_{10} \frac{a_1}{a_2}$$

Here $\qquad a_1 = 1$

$a_2 = 0\cdot1$

$n = 2$

$$\therefore \qquad \mathcal{E} = \frac{0\ 0591}{2} \log_{10} \frac{1}{0\cdot1} = 0\cdot02955 \text{ volt.}$$

(2) Eletrolytic Concentration Cells

A cell of this type consists of two identical electrodes in contact with two different solution containing the ions of the electrodes at different concentrations or activities. Since the activities of the reversible ions are different at two electrodes, they give different electrode potentials. The difference in electrode potentials gives rise to the emf of the cell.

Depending upon the way in which the two solutions of different concentrations are put in physical contact. two case arise.

(*i*) *When the solutions are in direct contact with each other.* In this case ions tend to diffuse and transfer of electrolyte from more concentrated solution to more dilute solution takes place. potential develops at the junction of two solutions which is called liquid-liquid junction potential. This is taken into account when computing the emf of the cell. This cells of this type are called **concentration cells with transference** or **concentration cells with liquid junction.**

(*ii*) *When the solutions are not in direct contact with [illegible] other.* Such cells have no liquid junctions are hence [illegible] transfer of electrolyte from one solutions to the other [illegible] They do not have liquid-liquid junction potentials. Such [illegible] cells are called **concentration cells without tran[illegible] concentration cells without liquid-liquid junction** [illegible]

Now we shall discuss both types of cells se[illegible] latter first.

(i) Electrolyte concentration cell without Transference Consider the cell

$$Pt \mid H_2\,(1\text{ atm}) \mid HCl\,(a_{\pm}) \mid AgCl\,(s) \mid Ag$$

which has the reactions

$$\tfrac{1}{2}H_2\,(1\text{ atm}) + AgCl\,(s) \rightleftharpoons H^+\,(a_+) + Cl^-\,(a_-) + Ag\,(s)$$

where (a_+) and (a_-) represent the activities of hydrogen and chlorine ions respectively in the HCl solution of mean ionic activity $(a_{\pm})$.

If two such cells having HCl solutions at different mean ionic activities are connected through their silver electrodes so as to oppose each other, the combined cell will be :

$$Pt/H_2(1atm)/HCl(a_{\pm})_1/AgCl(s)/Ag/AgCl(s)/HCl(a_{\pm})_2/H_2(1atm)/Pt$$

where $(a_{\pm})_2 > (a_{\pm})_1$. The overall cell reaction is simply the sum of the two reactions of two component cells.

Left hand cell $\quad \tfrac{1}{2}H_2(1atm) + AgCl(s) \rightleftharpoons Ag(s) + H^+(a_+)_1 + Cl^-(a_-)_1$

Right hand cell $\quad Ag(s) + H^+(a_+)_2 + Cl^-(a_-)_2 \rightleftharpoons \tfrac{1}{2}H_2(1atm) + AgCl(s)$

Overall cell reaction $\quad H^+(a_+)_2 + Cl^-(a_-)_2 \rightleftharpoons H^+(a_+)_1 + Cl^-(a_-)_1 \quad ...(7\cdot37)$

The overall cell reaction shows that no chemical change occurs. It only involves the transfer of HCl form mean activity $(a_{\pm})_2$ to $(\pm)_1$. Utilizing Eq. (7·12) with the fact that $\mathcal{E}°$ for such cells is zero, the emf of the cell is given by

$$\mathcal{E} = -\frac{RT}{\mathcal{F}} \ln \frac{(a_+)_1\,(a_-)_1}{(a_+)_2\,(a_-)_2}$$

$$= -\frac{RT}{\mathcal{F}} \ln \frac{(a_{\pm})^2_1}{(a_{\pm})^2_2}$$

$$= -\frac{2RT}{\mathcal{F}} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

or $$\mathcal{E} = \frac{2RT}{\mathcal{F}} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} \qquad ...(7\cdot38)$$

For a general case, when an electrolyte comprises of ν_+ cations and ν_- anions, Eq. (7·38) becomes

$$\mathcal{E} = -\frac{\nu}{\nu_{\pm}} \frac{RT}{n\mathcal{F}} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} \qquad ...(V\cdot39)$$

where $\nu = (\nu_+ + \nu_-)$ and n is the valence of the ion with respect to which the electrodes are reversible. The use of ν_+ or ν_- depends upon whether the outer electrodes of the cell are reversible to cations or anions respectively.

Eq. (7·39) gives the emf of the cell in terms of *mean ionic actitities*. If *activities* of electrolytes are known in place of *mean ionic activities*, Eq. (7·39) may be written as

where $(a_{\pm})_2 > (a_{\pm})_1$. The total emf of the cell will be the algebraic sum of left hand electrode potential (oxidation), right hand electrode potential (reduction), and liquid-liquid function potential. The liquid-liquid function potential arises due to the diffusion of ions across the boundary between two solutions from a higher to a lower concentration. The faster ions move across the boundary much ahead of those which move slowly and this leads to separation of charges. As the charges are separated in the form of double layer, a liquid-liquid function potential sets up.

To compute the total emf of the cell which is related to the net reaction which occurs when one faraday current is withdrawn. We shall write the changes at electrodes and at liquid function separately and then combine them. When one faraday current is withdrawn, the electrode reactions are

At left hand electrode	$Ag \rightarrow Ag^+ (a_+)_1 + e^-$
At right hand electrode	$Ag^+ (a_+)_2 + e^- \rightarrow Ag$
Net electrode reaction	$Ag^+ (a_+)_2 \rightarrow Ag^+ (a_+)_1$ ...(7·42)

If t_+ and t_- are the transport numbers of Ag^+ and NO_3^- ions respectively then on passing 1 faraday electricity through the cell, t_+ equivalent of Ag^+ ions will cross the liquid function from left to right and t_- equivalents of NO_3^- ions from right to left, as shown in Fig 7·7. The reactions at the liquid-liquid function are

$$t_+ \, Ag^+ (a_+)_1 \rightarrow t_+ \, Ag^+ (a_+)_2$$

or

$$(1-t_-) \, Ag^+ (a_+)_1 \rightarrow (1-t_-) \, Ag^+ (a_+)_2 \qquad ...(7·43)$$

and

$$t_- \, NO_3^- (a_-)_2 \rightarrow t_- \, NO_3^- (a_-)_1 \qquad ...(7·44)$$

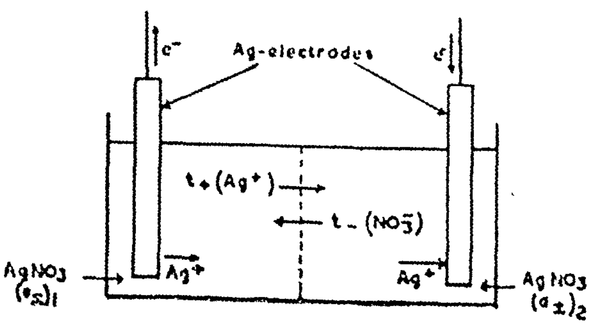

Fig. 7·7 Concentration cell with liquid-liquid junction.

The net cell reaction can be obtained by combining the net electrode reaction and the reaction at the liquid-liquid junction. Thus, adding Eq. (7·42), (7·43), and (7·44), we obtain

$$Ag^+ (a_+)_2 \rightarrow Ag^+ (a_+)_1$$
$$(1-t_-)\ Ag^+ (a_+)_1 \rightarrow (1-t_-)\ Ag^+ (a_+)_2$$
$$t_-\ NO_3^-(a_-)_2 \rightarrow t_-\ NO_3^- (a_-)_1$$

The net cell reaction

$$t_-\ Ag^+ (a_+)_2 + t_-\ NO_3^- (a_+)_2 \rightarrow t_-\ Ag^+ (a_+)_1 + t_-\ NO_3^- (a$$

or $t_- [Ag^+ (a_+)_2 + NO_3^- (a_+)_2] \rightarrow t_- [Ag^+ (a_+)_1 + NO_3^- (a_-)_1]$ ...(7·4

Thus, the net reaction involves the transfer of t_- equivaler of silver nitrate from a solution of higher activity to that of low activity for the passage of 1 faraday of electricity.

The emf of the cell can be obtained by applying Eq. (7·12) the reaction as reperesented by Eq. (7·45). $\mathcal{E}^\circ$ for the cell is ze and hence

$$\mathcal{E} = -\frac{RT}{\mathcal{F}} \ln \frac{[(a_+)_1 (a_-)_1]^{t_-}}{[(a_+)_2 (a_-)_2]^{t_-}}$$
$$= -t_- \frac{RT}{\mathcal{F}} \ln \frac{(a_+)_1 (a_-)_1}{(a_+)_2 (a_-)_2}$$
$$= -t_- \frac{RT}{\mathcal{F}} \ln \frac{(a_\pm)_1^2}{(a_\pm)_1^2} \quad \text{where } (a^2_\pm) = (a_+)(a_-)$$
$$= -2t_- \frac{RT}{\mathcal{F}} \ln \frac{(a_\pm)_1}{(a_\pm)_2}$$

or $$\mathcal{E} = +2t_- \frac{RT}{\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad ...(7·46)$$

In this case the electrodes are reversible to cations. If the electrodes are reversible to anions, *e.g.*, the following cell,

$$Ag \mid AgCl\ (s) \mid HCl\ (a_\pm)_1 \mid HCl\ (a_\pm)_2 \mid AgCl\ (s) \mid Ag$$

where $(a_\pm)_1 > (a_\pm)_2$, the emf of the cell would be

$$\mathcal{E} = 2t_+ \frac{RT}{\mathcal{F}} \ln \frac{(a_\pm)_1}{(a_\pm)_2} \qquad (7·47)$$

It should be noted that the transference number of the ionic species which appears in Eq. (7·46) and (7·47) are those ionic specicies to which the electrodes are not reverssible. For the general case, where an electrolyte comperises of ν_+ cations and ν_- anions, the ganeral from of cell emf is

$$\mathcal{E} = \pm t_\pm \frac{\nu}{\nu_\pm} \frac{RT}{n\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \qquad ...(7·4$$

where $\nu = (\nu_+ + \nu_-)$ and n is the valence of the ion to which the electrodes are reversible. It is seen that Eqs. (7·46) ... are consistent with the general form,

Eq. (7·48) represents the emf of the cell in terms of *mean ionic activities*. If *activities* of electrolytes are known in palce of *mean ionic activities*, Eq. (7·48) may be writhen as

$$\mathcal{E} = \pm\ t_{\pm} \frac{1}{\nu_{\pm}} \frac{RT}{n\mathcal{F}} \ln \frac{(a_{\pm})_2{}^{\nu}}{(a_{\pm})_1{}^{\nu}} \qquad \cdots(7{\cdot}49)$$

Since $a = (a_{\pm})^{\nu}$, Eq. (7·49) may be written as

$$\mathcal{E} = \pm\ t_{\pm} \frac{1}{\nu_{\pm}} \frac{RT}{n\mathcal{F}} \ln \frac{a_2}{a_1} \qquad \ldots(7{\cdot}50)$$

Example 8. *Calculate the emf of the following concentration cells with trnasference at 25°C.*

Cell I $\quad Pt \mid H_2(1atm \mid \underset{(a=0{\cdot}001)}{HCl} \mid \underset{(a=0{\cdot}1)}{HCl} \mid H_2(1atm) \mid pt$

Transference number of Cl^- ion is 0·160

Cell II $\quad Pb \mid PbSO_4\,(s) \mid \underset{(a\pm=0{\cdot}022)}{CuSO_4} \mid \underset{(a\pm=0{\cdot}0064)}{CuSO_4} \mid PbSo_4(s) \mid Pb$;

Transference number of Cu^{2+} ion is 0·370

Solution.

Cell I Since the extreme electrodes are reversible to cations and activites are given, we know that

$$\mathcal{E} = t_{-} \frac{1}{\nu_{+}} \frac{RT}{n\mathcal{F}} \ln \frac{a_2}{a_1} = t_{-} \frac{1}{\nu_{+}} \frac{2{\cdot}303\ RT}{n\mathcal{F}} \log_{10} \frac{a_2}{a_1}$$

Here
$t_{-} = 0{\cdot}160$
$\nu_{+} = 1$
$a_1 = 0{\cdot}001$
$a_2 = 0{\cdot}1$
$n = 1$

at 25°C. $\dfrac{2{\cdot}303\ RT}{\mathcal{F}} = 0{\cdot}0591$

$$\therefore \quad \mathcal{E} = 0{\cdot}160 \times \frac{0{\cdot}0591}{1} \log_{10} \frac{0{\cdot}1}{0{\cdot}001}$$
$$= 0{\cdot}160 \times 0{\cdot}0599 \times 2$$
$$= 0{\cdot}01889 \text{ volt.}$$

Cell II Since the extreme electrodes are reversible to anions and mean ionic activities are given, we know that

$$\mathcal{E} = -\ t_{+} \frac{\nu}{\nu_{-}} \frac{RT}{n\mathcal{F}} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} = -\ t_{+} \frac{\nu}{\nu_{+}} \frac{2{\cdot}303\ RT}{n\mathcal{F}} \log_{10} \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

Here $t_{+} = +\,0{\cdot}370$
$\nu = 2$ since $CuSO_4 \rightarrow Cu^{2+} + SO_4{}^{2-}$
$\nu_{+} = 1$
$n = 2$

at 25°C $2{\cdot}303 \dfrac{RT}{\mathcal{F}} = 0{\cdot}0591$

$(a_{\pm})_1 = 0{\cdot}022$
$(a_{\pm})_2 = 0{\cdot}0064$

$$\therefore \mathcal{E} = 0{\cdot}370 \times \frac{2}{1} \times \frac{0{\cdot}0591}{2} \log_{10} \frac{0{\cdot}0061}{0{\cdot}022}$$
$$= 0{\cdot}370 \times 0{\cdot}0591 \times 0{\cdot}5362$$
$$= 0{\cdot}01172 \text{ volt}$$

The Salt Bridge for ordinary laboratary purposes, the liquid-liquid junction potential can be eliminated or reduced to negligible amount if the solutions two half cells are connected by means of a salt bridge as shown in Fig. 7·8. The salt bridge is an inve

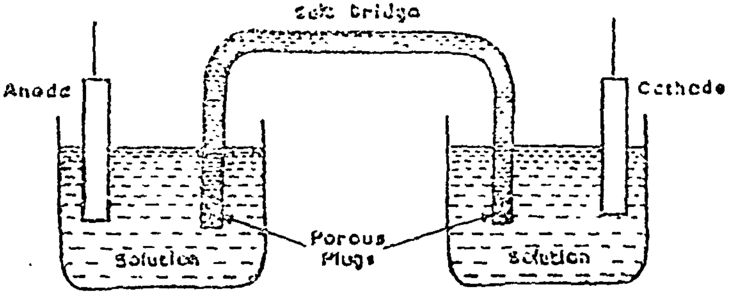

Fig. 7·8 Salt bridge

rted U-tube containing saturated solution of either KCl or NH_4NO_3. The electrolyte is generally set in *agar-agar* gel. The ends of the tube are often plugged with a porous material such cotton or glass wool to prevent the excessive diffusion. The concentration of the salt solution must be very high of the solution function so that almost whole of the current is carried out by the ions of the salt and hence the effect of difference between the two electrode solutions is almost suppressed. This for this reason that saturated solution of the salt is used in making the salt bridge. The exact mechanism of the salt bridge is not yet clearly known but it is supposed to be associated with the fact that the transport numbers of cations and anions of the salt in the bridge almost equal. Thus, the potential developed between one solution and the potential between other solution and bridge solution, being approximately equal in magnitude but opposite in sign, almost cancel out.

Electrolyte Concentration cells with Eliminated Liquid-Liquid junction Potentials Consider the following cell

$$Ag \mid Ag\,NO_3\,(a_\pm)_1 \parallel Ag\,NO_3\,(a_\pm)_2 \mid Ag$$

where $(a_\pm)_2 > (a_\pm)_1$. Here the two half cells are joined via salt bridge. The electrode reaction are

At left hand electrode $\quad Ag \rightarrow Ag^+\,(a_+)_1 + e^-$

At right hand electrode $\quad Ag^+\,(a_+)_2 + e^- \rightarrow Ag$

Net electrodes reaction $\quad Ag^+\,(a_+)_2 \rightarrow Ag$

Since liquid-liquid junction potential is eliminated with the help of salt bridge, Eq. (7·51) may be taken as the overall cell reaction. Utilizing Eq. (7·12) with the fact that $\mathcal{E}^\circ$ for such cells is zero, the emf of the cell is given by

$$\mathcal{E} = \frac{RT}{\mathcal{F}} \ln \frac{(a_\pm)_1}{(a_\pm)_2} = \frac{RT}{\mathcal{F}} \ln \frac{(a_+)_2}{(a_+)_1} \quad \cdots(7{\cdot}52)$$

By definition $\quad (a_\pm)^2 = a_+ a_-$

If it is assumed that $a_+ \approx o_-$

then $\quad a_+ \approx a_-$

Hence Eq. (7·52) may be written as

$$\mathcal{E} = \frac{RT}{\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \quad \ldots(7{\cdot}53)$$

For the general case,

$$\mathcal{E} = \pm \frac{RT}{n\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \quad \ldots(7{\cdot}54)$$

where n is the valence of the ion to which the electrodes are reversible. When the electrodes are reversible to cations, the positive sign is applicable and when the electrodes are reversible to anions, the negative sign is applicable.

Example 9. *Calculate the emf of the following concentrations cells at 25°C.*

Cell I. $\quad$ Zn | Zn SO_4 ($a_\pm$ = 0·01) || Zn SO_4 ($a_\pm$ = 0·1) | Zn

Cell II. $\quad$ Ag | Ag Cl (*s*) | Li Cl ($a_\pm$ = 0·2) || Li Cl ($a_\pm$ = 0·01) | Ag Cl (*s*) | Ag

Solution.

Cell I Since the electrodes are reversible to cations, we know that

$$\mathcal{E} = \frac{RT}{n\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = \frac{2{\cdot}303\ RT}{n\mathcal{F}} \log_{10} \frac{(a_\pm)_2}{(a_\pm)_1}$$

Here $\quad n = 2$

$(a_\pm)_1 = 0{\cdot}01$

$(a_\pm)_2 = 0{\cdot}1$

at 25°C $\quad \dfrac{2{\cdot}303\ RT}{\mathcal{F}} = 0{\cdot}0591$

$$\therefore \quad \mathcal{E} = \frac{0{\cdot}0591}{2} \log_{10} \frac{0{\cdot}1}{0{\cdot}01}$$

$$= \frac{0{\cdot}0591}{2} = 0{\cdot}02955 \text{ volt.}$$

Cell II Since the electrodes are reversible to anions, we know that

$$\mathcal{E} = -\frac{RT}{n\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = \frac{2{\cdot}303\ RT}{n\mathcal{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

Here $n = 1$

$(a\pm)_1 = 0{\cdot}2$

$(a\pm)_2 = 0{\cdot}01$

at 25°C $\dfrac{2{\cdot}303\ RT}{\mathcal{F}} = 0{\cdot}0591$

$$\therefore \qquad \mathcal{E} = -\frac{0{\cdot}0591}{1}\log_{10}\frac{0{\cdot}01}{0{\cdot}2}$$

$$= 0{\cdot}0591\ \log_{10}\frac{0{\cdot}2}{0{\cdot}01} = 0{\cdot}0591\times 1{\cdot}3010$$

$$= 0{\cdot}07688 \text{ volt}$$

Calculation of liquid-liquid Junction Potential The net emf of a cell with transference is the algebraic sum of the electrode potentials and the liquid-liquid junction potential. Thus,

$$\mathcal{E}_{cell} = \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_j$$

where $\mathcal{E}_1$ is the oxidation potential of the left hand electrode, $\mathcal{E}_2$ is the reduction potential of the right hand electrode, and $\mathcal{E}_j$ is the liquid-liquid junction potential. The liquid-liquid junction potential may be given by

$$\mathcal{E}_j = \mathcal{E}_{cell} - (\mathcal{E}_1 + \mathcal{E}_2) \qquad \ldots(7{\cdot}55)$$

Now consider the following cell with transference

$$Ag \mid Ag\,NO_3\,(a_\pm)_1 \mid Ag\,NO_3\,(a_\pm)_2 \mid Ag$$

The emf of the cell is given by Fq. (7·46),

$$\mathcal{E}_{cell} = 2t_- \frac{RT}{\mathcal{F}}\ln\frac{(a_\pm)_2}{(a_\pm)_1} \qquad \ldots(7.56)$$

Now if the liquid-liquid junction of the above cell is eliminated with the help of the salt bridge, the emf of the cell will be the algebraic sum of $\mathcal{E}_1$ and $\mathcal{E}_2$. Thus, from Eq. (7·53) we can write

$$\mathcal{E} = (\mathcal{E}_1 + \mathcal{E}_2) = \frac{RT}{\mathcal{F}}\ln\frac{(a_\pm)_2}{(a_\pm)_1} \qquad \ldots(7{\cdot}57)$$

Substituting Eqs. (7·56) and (7·57) in Eq. (7·55), we get

$$\mathcal{E}_j = 2t_- \frac{RT}{\mathcal{F}}\ln\frac{(a_\pm)_2}{(a_\pm)_1} - \frac{RT}{\mathcal{F}}\ln\frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= (2t_- - 1)\frac{RT}{\mathcal{F}}\ln\frac{(a_\pm)_2}{(a_\pm)_1}$$

Since $\qquad t_+ = 1 - t_-$

$$(2t_- - 1) = t_- + t_- - 1 = t_- - (1 - t_-) = (t_- - t_+)$$

$$\therefore \quad \mathcal{E}_j = (t_- - t_+)\frac{RT}{\mathcal{F}}\ln\frac{(a_\pm)_2}{(a_\pm)_1} \qquad (7{\cdot}58)$$

from this equtaion it is evident that the sign of $\mathcal{E}_j$ depends on the values of t_+ and t_-. If t_+ is very nearly equal to t_-, the value of $\mathcal{E}_j$ will be very small.

Determination of pH.

The pH of a solution may be determined easily by emf measurements. A cell is set up in which an indicator electrode reversible to H^+ ions is immersed in the solution whose pH value is to be determined and the other reference electrode is generally calomel electrode. The calomel electrode is either immersed into the solution directly or connected with the help of a salt bridge. The emf of the cell is determined, using potentiometer. The electrode potential of calomel electrode when subtracted from emf of the cell gives the electrode potential of the indicator electrode. From this value, the pH of the solution can be evaluated using a suitable electrode potential equation. Most commonly used indicator electrodes reversible to H^+ ions are (*i*) hydrogen electrode, (*ii*) quinhydrone electrode and (*iii*) glass electrode. Now we shall discuss the use of these electrodes for the determination of pH separately.

(*i*) **Use of Hydrogen Electrode.** The expression for the electrode potential of hydrogen electrode as given by Eq. (7·30) may be written as

$$H_2 = -\frac{RT}{\mathcal{F}} \ln a_{H^+}$$

or $$H_2 = -\frac{2{\cdot}303\, RT}{\mathcal{F}} \log_{10} a_{H^+}$$

Since $$-\log_{10} a_H = \text{pH}$$

$$\therefore \quad \mathcal{E}_{H_2} = \frac{2{\cdot}303\, RT}{\mathcal{F}} \text{pH} \qquad ...(7{\cdot}59)$$

when hydrogen electrode is immersed in the solution whose pH is to be determined is coupled with saturated calmol electrode, the cell is formulated as

Pt | H_2 (1 atm) | solution of unknown pH || KCl (satd soln) | $Hg_2\,Cl_2(s)$ | Hg

The emf of the cell is given by

$$\mathcal{E}_{cell} = \mathcal{E}_{H_2} - \mathcal{E}_{cal}$$
$$= \frac{2{\cdot}303\, RT}{\mathcal{F}} \text{pH} - \mathcal{E}_{cal}$$

At 25°C, $\frac{2 \cdot 303\, RT}{\mathcal{F}} = 0 \cdot 0591$

$$\therefore \qquad \mathcal{E}_{cell} = 0 \cdot 0591\ pH - \mathcal{E}_{cal}$$

or
$$pH = \frac{\mathcal{E}_{cell} + \mathcal{E}_{cal}}{0 \cdot 0591} \qquad ...(7 \cdot 60)$$

In this case we have used saturated calomel electrode, the electrode potential of which at 25°C is $-0 \cdot 2415$ volt. Substituting in Eq. (7·60) we get

$$pH = \frac{\mathcal{E}_{cell} - 0 \cdot 2415}{0 \cdot 0591} \qquad ...(7 \cdot 61)$$

If a calomel electrode other than the saturated calomel electrode is used, the appropriate value of $\mathcal{E}_{cal}$ is to be substitued in Eq. (7·60).

Example 9. *At 25°, the cmf of the cell*

$$Pt \mid H_2 \ (1\ atm) \mid \begin{matrix} solution\ of \\ unknown\ pH \end{matrix} \parallel KCl\ (satd\ soln) \mid Hg_2Cl_2\ (s) \mid Hg$$

is 0·445 volt. Calculated the pH of the solution.

Solution We know that for such a cell

$$pH = \frac{\mathcal{E}_{cell} - 0 \cdot 2415}{0:0591}$$

Here $\qquad \mathcal{E}_{cell} = 0 \cdot 445$ volt

$$\therefore \qquad pH = \frac{0.445 - 0 \cdot 2415}{0 \cdot 0591} = 3 \cdot 44$$

(*ii*) **Use of Quinhydrone Electrode.** Quinhydrone is a loose chemical compound which contains quinone and hydroquinone in equimolecular quantities. If some quantity of quinhydrone is added to a solution whose pH is to be determined and a platinum wire is dipped into it, an electrode is set up. Since hydroquinone is a reduction product of quinone, this electrode is oxidation-reduction or redox electrode. The cell is repaesented as

Pt | Solution sated with quinhydrone

and the oxidation reaction is

$$\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} = \underset{\text{quinone}}{C_6H_4O_2} + 2H^+ + 2\,e^-$$

The oxidation electrode potential is given by

$$\mathcal{E}_Q = \mathcal{E}^\circ_Q - \frac{RT}{2\mathcal{F}} \ln \frac{a_{quinone} \times a_{H^+}}{a_{hydroquinone}}$$

Since quinone and hydroquinone are present in equimolecular quantities, $a_{\text{quinone}} = a_{\text{hydroquinone}}$; Eq. (7·62) reduces to

$$\mathcal{E}_Q = \mathcal{E}_Q^{\circ} - \frac{RT}{2\mathcal{F}} \ln a_{H}^{2+}$$

$$= \mathcal{E}_Q^{\circ} - \frac{RT}{\mathcal{F}} \ln a_{H^+}$$

$$= \mathcal{E}_Q^{\circ} - \frac{2{\cdot}303\, RT}{\mathcal{F}} \log_{10} a_{H^+}$$

or

$$\mathcal{E}_Q = \mathcal{E}^{\circ}_Q + \frac{2{\cdot}303\, RT}{\mathcal{F}} \text{pH} \qquad \text{...(7·63)}$$

This equation shows that quinhydrone electrode is reversible to H^+ ions and behaves as a form of hydrogen electrode. At 25°C. the value of $\mathcal{E}_Q^{\circ}$ is found to be 0·6994 volt and the value of 2·303 $RT/\mathcal{F}$ is 0·0591. Hence Eq. (7·63) may be written as

$$\mathcal{E}_Q = 0{\cdot}6994 + 0{\cdot}0591\, \text{pH} \qquad \text{...(7·64)}$$

The pH of the solution is determined by combining quinhydrone electrode with a calomel electrode and measuring the emf of the complete cell using potentiometer. The complete cell may be represented as

Hg—Hg_2Cl_2 | KCl (soln) ‖ Solution (unknown pH) | Pt
‖ Saturated with Quinhydrone

The emf of the cell is given by

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cal}} - \mathcal{E}_Q$$

$$= \mathcal{E}_{\text{cal}} - 0{\cdot}6994 - 0{\cdot}0591 \text{ pH (at 25°C)}$$

or

$$\left(\text{pH} = \frac{\mathcal{E}_{\text{cal}} - \mathcal{E}_{\text{cell}} - 0{\cdot}6994}{0{\cdot}0591} \right) \qquad \text{...(7·65)}$$

Thus, by measuring $\mathcal{E}_{\text{cell}}$ and substituting the appropriate value of $\mathcal{E}_{\text{cal}}$, the pH of the solution can be evaluated.

Quinhydrone electrode is very usefui in pH measurements. It can be used in presence of reducible substances such as Cu, Zn, Pb, Cd salts, unsaturated acids, etc. However, it gives erratic values in presence of NH_4^+ ions. Upto pH = 7·1, the electrode acts as positive electrode against normal calomel electrode and above this value it starts acting as negative electrode. In a solution of pH$>$8·5, oxygen of the air reacts with hydroquinone and the electrode equilibrium is disturbed giving erratic results. Thus, in more alkaline solution this electrode should not be used.

Example 10. *The emf of the cell*

$HgHg_2Cl_2(s)$ / KCl (satd) // with Quinhydrone / Pt is 1·16 volt at 25°C. If $\mathcal{E}$ cal at 25°C. is—0·2415 volt, calculate the pH of the solution.

Solution. We know that

$$pH = \frac{\mathcal{E}_{cal} - \mathcal{E}_{cell} - 0{\cdot}6994}{0{\cdot}0591}$$

Here $\mathcal{E}_{cal} = -\ 0{\cdot}2415$ volt

$\mathcal{E}_{cell} = -1{\cdot}16$ volt

$$\therefore \quad pH = \frac{-0{\cdot}2315-(-1{\cdot}16)-0{\cdot}6994}{0{\cdot}0591} = \frac{0{\cdot}2191}{0{\cdot}0591}$$

$$= 3{\cdot}707$$

(*iii*) **Use of Glass Electrode.** It has been established experimentailly that when a solution is separated from other solution at different H^+ ion activity by a glass membrane, a potential exists across the membrance which depends primarily on the difference of the activities of H^+ ions in the two solutions. If the activity of H^+ ions in one of the solution is kept constant and in the other is changed, the potential of the glass electrode is given by

$$\mathcal{E}_G = \mathcal{E}^\circ_G - \frac{RT}{\mathcal{F}} \ln a_{H^+}$$

$$= \mathcal{E}^\circ_G - \frac{2{\cdot}303\ RT}{\mathcal{F}} \log_{10} a_{H^+}$$

or $$\mathcal{E}_G = \mathcal{E}^\circ_G + \frac{2{\cdot}303RT}{\mathcal{F}}\ pH \qquad ...(7{\cdot}66)$$

where $\mathcal{E}^\circ G$ is a constant for a particular glass electrode. From Eq. (7·66), it is evident that glass electrode is also reversible to H^+ ion, and can be used to measure pH of solutions.

A glass electrode consists of a tube, made of special glass of very high resistance and low melting point, which ends in a thin-walled bulb at the bottom. The bulb is filled with a solution of constant pH and an electrode of definite potential is dipped into it. For this purpose generally (*i*) silver-silver chloride electrode with 0·1 *M* HCl solution or (*ii*) a platinum wire immersed in a buffer solution (0·05 *M* Potassium hydrogen phthalate) saturated with qunihydrone is used. Fig. 7·9 shows a glass electrode contaning silver-silver chloride electrode 0·1 with *M* HCl solution. The cell is represented as

Ag | AgCl(*s*) | HCl (0·1*M*)—glass

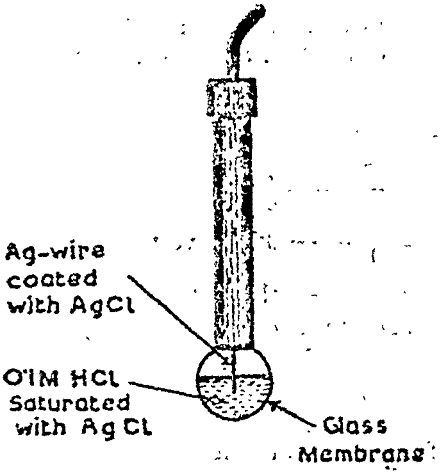

Fig 7·9 Glass Electrode

To measure the pH of a solution, the glass electrode is immersed in it and is coupled with calomel electrode. The cell may be formulated as

Ag | AgCl (s) | HCl (0·1 M) | glass | Solution of unknown pH | Calomel Electrode

The emf of the cell is determined with a special vacuum tube potentiometer because the resistance of the thin wall of the bulb is very high and hence ordinary potentiometer can not be used. The emf of the cell is

$$\mathcal{E}_{cell} = \mathcal{E}_G - \mathcal{E}_{cal}$$

$$= \mathcal{E}^\circ_G + \frac{2 \cdot 303 RT}{\mathcal{F}} \text{pH} - \mathcal{E}_{cal}$$

$$= \mathcal{E}^\circ_G + 0 \cdot 0591 \text{ pH} - \mathcal{E}_{cal} \text{ (at 25°C)}$$

or: $$\text{pH} = \frac{\mathcal{E}_{cell} + \mathcal{E}_{cal} - \mathcal{E}^\circ_G}{0 \cdot 0591} \quad \ldots(7 \cdot 67)$$

As already stated, $\mathcal{E}^\circ_G$ is a constant for a particular electrode, it is determined separately. Thus, knowing the value of $\mathcal{E}_{cal}$ and $\mathcal{E}^\circ_G$, the pH of the solution can be evaluated.

Glass electrodes are widely used for pH determinations because they are not positioned easily and remain unaffected even by strong oxidising and reducing agents.

Determination of Transport Number of Ions from EMF Measurements. The transport number of ions can be determined by measuring the emf of a concentration cell composed of two solutions of the salt containing the ions in question at different activities. For example, to determine the transport number of Ag^+ and NO_3^- ions, the following cell is set up

$$Ag \mid AgNO_3\,(a_1) \mid AgNO_3\,(a_2) \mid Ag \qquad \text{...(7·68)}$$

The emf of the cell is measured which is related to the transport number of NO_3^- by Eq. (7·50), *i.e.*,

$$\mathcal{E} = t_- \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} \qquad \text{...(7·69)}$$

Thus, knowing a_1, a_2 and $\mathcal{E}$, the transport number t_- can be evaluated.

Example 11. *The emf of the concentration cell*

$$Ag \mid AgNO_3\,(a = 0{\cdot}00096) \mid AgNO_3\,(a = 0{\cdot}085) \mid Ag$$

is 0·0556 volt at 25°C. Calculate the transport number of Ag^+ and NO_3^- ions.

Solution. Since the extreme electrodes are reversible to cations we know that

$$\mathcal{E} = t_- \frac{1}{\nu_+ n} \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} = t_- \frac{1}{\nu_+} \frac{2{\cdot}303\,RT}{n\mathcal{F}} \log_{10} \frac{a_2}{a_1}$$

Here $\mathcal{E} = 0{\cdot}0556$ volt

$\nu_+ = 1$

$n = 1$

$a_1 = 0{\cdot}00096$

$a_2 = 0{\cdot}085$

At 25°C, $\frac{2{\cdot}303\,RT}{\mathcal{F}} = 0{\cdot}0591$

$$\therefore \quad 0{\cdot}0556 = t_- \times 0{\cdot}0591 \log_{10} \frac{0{\cdot}085}{0{\cdot}00096}$$

$$= t_- \times 0{\cdot}0591 \times 1{\cdot}9471$$

or $\quad t_- = \frac{0{\cdot}0556}{0{\cdot}0591 \times 1{\cdot}9471} = 0{\cdot}483$

Since $\quad t_+ = 1 - t_-$

$$= 1 - 0{\cdot}483 = 0{\cdot}517$$

$\therefore$ The transport number of Ag_+ ions $= 0{\cdot}517$ and NO_3^- ions $= 0{\cdot}483$

There is another method of determining transference numb of ions. This method is based on the measurements of emf s

concentration cells with and without transference containing the same electrolytes at the same activities. For example, consider the following cells :

(*i*) Pt | H_2 (1 atm) | HCl | HCl | H_2 (1 atm) | Pt
(a_1) (a_2)

(*ii*) Pt | H_2 (1 atm) | HCl | AgCl (*s*) | Ag | AgCl (*s*) | HCl |
(a_1) (a_2)
H_2 (1 atm) | Pt

Utilizing Eq. (7·50), the emf $\mathcal{E}_1$ of the concentration cell with transference (*i*) is given by

$$\mathcal{E}_1 = t_- \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} \qquad ...(7·70)$$

and utilizing Eq. (7·41), emf $\mathcal{E}_2$ of the concentration cell without transference (*ii*) is given by

$$\mathcal{E}_2 = \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} \qquad ...(7·71)$$

Dividing Eq. (7·70) by Eq. (7·71), we get

$$\frac{\mathcal{E}_1}{\mathcal{E}_2} = t_- \qquad ...(7·72)$$

Thus, by measuring $\mathcal{E}_1$ and $\mathcal{E}_2$, the transference number t_- can be evaluated.

For a general case, Eq. (7·72) may be written as

$$\frac{\mathcal{E}_1}{\mathcal{E}_2} = t_{\mp} \qquad ...(7·73)$$

If outer electrodes are reversible to cations the transference number refers to anion *i.e.*, t_- and if the outer electrodes are reversible to anions, the transference number refers to cation *i.e.*, t_+.

TEST YOUR KNOWLEDGE

1. Complete the following :

(*i*) $... = -n\mathcal{E}\mathcal{F}$

(*ii*) $\mathcal{E} = ... + T \left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$

(iii) $\ldots = n\mathfrak{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P$

(iv) $\mathcal{E} = \ldots - \frac{RT}{n\mathfrak{F}} \ln \frac{({}^{a}C)^{c} \times ({}^{a}D)^{d}}{({}^{a}A)^{a} \times ({}^{b}B)^{a}}$

(v) At 25°C, $\mathcal{E} = \mathcal{E}^\circ - \frac{\ldots}{n} \log_{10} \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$

(vi) $\mathcal{E}_{Cu} = \mathcal{E}^\circ_{Cu} - \frac{RT}{\ldots} \ln a_{Cu^{2+}}$

(vii) $\mathcal{E}_{Cl} = \mathcal{E}^\circ_{Cl_2} \ldots \frac{RT}{n\mathfrak{F}} \ln a_{Cl^-}$

(viii) $\mathcal{E}_{red} = \mathcal{E}^\circ_{red} + \frac{RT}{n\mathfrak{F}} \ldots$

(ix) $\mathcal{E}_{Cal} = \mathcal{E}^\circ_{cal} + \frac{RT}{2\mathfrak{F}} \ldots$

(x) $\mathcal{E}_{Ag-AgCl} = \mathcal{E}^\circ_{Ag-AgCl} + \frac{RT}{\mathfrak{F}} \ldots$

(xi) $\mathcal{E} = \pm \frac{\nu}{\nu_\pm} \frac{RT}{n\mathfrak{F}} \ln \ldots$

(xii) $\mathcal{E} = \pm \frac{1}{\nu_\pm} \frac{RT}{n\mathfrak{F}} \ln \ldots$

(xiii) $\mathcal{E} = \pm\ t \ldots \frac{\nu}{\nu_\pm} \frac{RT}{n\mathfrak{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$

(xiv) $\mathcal{E} = \ldots\ t_+ \frac{1}{\nu_-} \frac{RT}{n\mathfrak{F}} \ln \frac{a_2}{a_1}$

(xv) $\mathcal{E} = \pm \frac{RT}{n\mathfrak{F}} \ln \ldots$

(xvi) $\mathcal{E}_j = (\ldots - t_+) \frac{RT}{n\mathfrak{F}} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$

(xvii) $\mathcal{E}_{H_2} = \ldots$ pH

(xviii) $\mathcal{E}_Q = \mathcal{E}^\circ_Q + \frac{2{\cdot}303\ RT}{\mathfrak{F}} \ldots$

(xix) $\ldots = \frac{\mathcal{E}_{cal} + \mathcal{E}_{cal} - \mathcal{E}^\circ_G}{0{\cdot}0591}$

(xx) $\frac{\mathcal{E}_1}{\mathcal{E}_2} = \ldots$

2. **Give a term for each of the following :**

   (*i*) Cell used for converting chemical energy into electrical energy.
   (*ii*) The overall chemical reaction in a electrochemical cell.
   (*iii*) The chemical reaction at one electrode.
   (*iv*) Property by virtue of which a metal tends to go into solution in the form of positive ions.
   (*v*) Electrodes having oxidised and reduced states in equilibrium.
   (*vi*) The potential of an electrode when the substances involved are at unit activity.
   (*vii*) Electrode potential based on the electrode oxidation reaction.
   (*viii*) The cell in which the emf arises due to transfer of matter from one region to another region of the cell.
   (*ix*) A potential existing across the interface of two liquid solutions.

3. **Fill in the blanks with appropriate words :**

   (*i*) The electrode from which electrons pass to the outer circuit is called negative electrode or...
   (*ii*) Oxidation occurs at..., while reduction at......
   (*iii*) If $P > \pi$, the electrode is... charged, and when $P < \pi$, the electrode is...charged.
   (*iv*) In the formulation of a cell, the anode half cell is written on the... hand side and cathode half cell on the...hand side.
   (*v*) The potential of normal hydrogen electrode is taken arbitrarily equal to...
   (*vi*) The...value of electrode oxidation potential shows that oxidation occurs spontaneously at the electrode.
   (*vii*) The reduction potentials can be obtained by reversing the sign of... potential.
   (*viii*) The emf of a cell is equal to the algebraic sum of...potential of left hand electrode and...potential of right hand electrode.
   (*ix*) The emf of a cell is equal to the...of oxidation potentials of two electrodes.
   (*x*) The calomel electrode containing saturated solution of KCl is called... electrode.
   (*xi*) The electrolyte concentration cell is...transference when two solutions are in direct contact and...transference when an intermediate electrode is introduced between the two solutions.

KEY

1. (*i*) ΔG, (*ii*) $-\Delta H/n\mathfrak{F}$, (*iii*) ΔS, (*iv*) $\mathcal{E}^\circ$. (*v*) 0·0591 (*vi*) $2\mathfrak{F}$, (*vii*) $+$, (*viii*) $\ln \frac{a_{ox}}{a_{red}}$, (*ix*) $\ln (a_{Cl^-})^2$ (*x*) $\ln a_{Cl^-}$ (*xi*) $(a_\pm)_2/(a_\pm)_1$, (*xii*) a_2/a_1, (*xiii*) $\mp$ (*xiv*) $-$, (*xv*) $(a_\pm)_2/(a_\pm)_1$ (*xvi*) t_-, (*xvii*) $2{\cdot}303\ RT/\mathfrak{F}$, (*xviii*) pH, (*xix*) pH, (*xx*) $t_\pm$

(i) Electrochemical cell or Galvanic cell, (ii) Cell reaction (iii) Half cell reaction, (iv) Solution pressure. (v) Redox electrodes (vi) Standard electrode potential, (vii) Oxidation potential, (viii) Concentration cell (ix) Liquid-liquid junction potential.

(i) anode, (ii) anode, cathode, (iii) negatively, positively, (iv) left, right (v) zero, (vi) positive (vii) oxidation, (viii) oxidation, reduction, (ix) reference (x) saturated calomel (xi) with, without.

QUESTIONS

What is an electrochemical or galvanic cell ? Describe Daniell cell and its function. What is the source of energy in this cell ?

What are reversible and irreversible cells ? Give one example of each cell.

Describe potentiometric method for measuring emf of a cell.

What are the requirements of a standard cell ? Describe Weston standard cell in detail.

Describe Nernst solution pressure theory. What is the modern theory of electrode potential ?

Write a note on notation and sign convention of electrochemical cells.

What do you understand by a 'reversible electrode' ? Describe various types of reversible electrodes.

What is Nernst equation ? Show how this equation is used in calculating the emf of a cell ?

What is single electrode potential ? Obtain an expression for the potential of an electrode.

What are redox electrodes ? Give examples. Obtain an expression for the redox potential of an electrode.

What are 'standard oxidation potentials' ? Give their significance. How the standard oxidation potential of an electrode can be obtained ?

What are reference electrodes ?. Describe the construction and working of (a) hydrogen (b) calomel and (c) Ag—Ag Cl electrode.

What are concentration cells ? Obtain an expression for the emf an electrode concentration cell.

What do you understanding by electrolyte concentration cells ? Derive expression for the emf of a concentration cell without transference when (i) the electrodes are reversible to cations and (ii) the electrodes are reversible to anions.

Derive expression for the emf of a concentration cell with transference (i) when the electrodes are reversible to cations and (ii) when the electrodes are reversible to anions.

Derive expressions for the emf of a concentration cell when the liquid liquid junction potential is eliminated with the help of salt bridge ... of (i) electrodes ... and (ii) electrodes ...

9. Describe quinhydrone electrode and show how it is used in the measurement of pH of a solution.

20. Describe glass electrode and discuss how it is used in the measurement of pH of a solution.

21. How transport number of ions can be determined by emf method ?

22. The emf of the cell

$$Pt \mid H_2 \mid HCl\ (a = 1\cdot0) \mid AgCl(s) \mid Ag$$

is 0·2224 volt at 25°C and its temperature coefficient is $-6\cdot45 \times 10^{-4}$ volt deg^{-1}. Calculate ΔG, ΔH and ΔS for the reaction occurring in the cell.

[Ans. $\Delta G = -5140$ cal, $\Delta H = -9580$ cal, $\Delta S = -14\cdot9$ cal deg^{-1}]

23. Calculate the emf of the following cell at 25°C

$$Zn \mid Zn^{2+}\ (a = 0\cdot012) \parallel H^+\ (a = 0\cdot01) \mid H_2\ (1\ atm) \mid Pt$$

The standard emf of this cell is 0·7618 volt.

[Ans. 0·~~237~~ volt] ·777

24. Calculate the oxidation potentials of the following electrodes at 25°C.

(i) $Pt \mid H_2\ (1\ atm) \mid H^+\ (a = 0\cdot08)$ $\mathcal{E}^\circ H_2 = 0$

(ii) $Cu \mid Cu^{++}\ (a = 0\cdot12)$ $\mathcal{E}^\circ Cu = -0\cdot337$ volt.

(iii) $Pt \mid Fe^{2+}\ (a = 0\cdot018), Fe^{3+}\ (a = 0\cdot09)$ $\mathcal{E}^\circ_{redox} = -0\cdot771$ volt.

(iv) $(Pt—Ir) \mid Cl_2\ (1\ atm) \mid Cl^-\ (a = 0\cdot2)$ $\mathcal{E}^\circ Cl_2 = -1\cdot3595$ volt.

[Ans. (i) 0·0649 volt (ii) —0·31 volt (iii) —0·73 volt (iv) 1·40 volt]

25. Calculate the potential of the following concentration cell at 25°C,

$$\underset{(a = 5\cdot0)}{Pb\ (Hg)} \mid Pb(NO_3)_2 \mid \underset{(a = 0\cdot05)}{Pb\ (Hg)}$$

[Ans. 0·02955 volt]

26. Calculate the emf of the following cell at 25°C.

$$Cd \mid \underset{a = 0\cdot004}{CdSO_4}\ (s) \mid PbSO_4(s) \mid Pb \mid PbSO_4(s) \mid \underset{(a = 0\cdot4)}{CdSO_4} \mid Cd$$

[Ans. 0·1182 volt]

27. Calculate the *emf of the following cell at 25°C.*

$$Ag \mid AgCl\ (s) \mid \underset{(a = 0\cdot2)}{NaCl} \mid Na(Hg) \mid \underset{(a = 0\cdot001)}{NaCl} \mid AgCl(s) \mid Ag$$

[Ans. 0·1360 volt]

28. Calculate the emf of the following concentration cells with transference at 25°C.

(i) $Ag \mid AgNO_3\ (a = 0\cdot005) \mid AgNO_3\ (a = 0\cdot05) \mid Ag$

The transference number of NO_3^- ion is 0·535)

(ii) $Hg \mid Hg_2SO_4\ (s) \mid \underset{(a = 0\cdot1)}{CdSO_4} \mid \underset{(a = 0\cdot005)}{CdSO_4} \mid Hg_2SO_4\ (s) \mid Hg$

The transference number of Cd^{2+} ion is 0·356.

[Ans. (i) 0·0699 volt, (ii) 0·04841 volt]

29. Calculate the emf of the following concentration cells at 25°C.

(i) $Cd \mid CdSO_4\ (a\pm = 0\cdot003) = CdSO_4\ (a\pm = 0\cdot03) \mid Cd$

(ii) $Ag \mid AgBr(s) \mid Br^-\ (a\pm = 0\cdot72) = Br^-\ (a\pm = 0\cdot072) \mid AgBr(s) \mid Ag$

[Ans. (i) 0·02955 volt (ii) (0·0591 volt]

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
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12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
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83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
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·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20